

IMPACT OF Mn²⁺ IONS ON MICRO-STRUCTURAL, LUMINESCENCE PROPERTIES OF ZnS-MoS₂ NANOCOMPOSITES FOR OPTOELECTRONICS

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ABSTRACT

Bottom-up hydrothermal synthesis was used to prepare semiconducting natured undoped and Mn²⁺ doped nanocomposites of ZnS-MoS₂. XRD -X-ray diffraction analysis, DRS- diffuse reflection spectroscopy spectrophotometer, FT-IR-Fourier transform infrared spectroscopy, SEM-scanning electron microscopy, and PL-photoluminescence techniques were used to characterize the structural, optical absorption, morphological, IR spectral, and luminescence properties of prepared powder samples. The average crystallite size of prepared nanocomposites ranged between 12 and 20 nm. The FT-IR spectra were used to examine the molecular vibrations and various functional groups contained in the prepared samples. Surface morphology analyses show the presence of spherical-shaped ZnS flakes and hexagonal MoS₂ flakes. The energy bandgap decreases as the quantity of Mn²⁺ doping in the host lattice increases, showing the quantum confinement of prepared samples. The PL data indicates a characteristic luminescence peak in the yellow-orange region at 585 nm.

Keywords: ZnS, MoS₂, Mn²⁺, Nanocomposite, Photoluminescence

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INTRODUCTION

Due to extensive size dependant features, low-dimensional semiconductors are generating a lot of attention among fundamental scientific, technical, and industry researchers these days. When the size of materials is reduced to nanometre size, then the ratio of surface to volume is increased and takes place the quantum confinement effect, their structural and optical characteristics change significantly due to this quantum confinement.^{1,2} At present, nano semiconducting materials play an important role in predicting new features and potential applications in a variety of industries. Nanocomposite materials having semiconducting nature comprised of two or more unique ingredient materials are commonly utilized to modify structural, electrical, and optical characteristics, specifically in the domain of electronic technology. Nanocomposites are often multiphase materials with higher stable thermal property photocatalytic activity than ZnS and MoS₂.^{3,4}

The sulfur sourced ZnS and MoS₂ are agile materials that are frequently employed as generally used host materials for luminous applications like solid-state lubrication, sensing, water splitting, optoelectronic devices, catalytic-element by desulfurization and energy storage (capacitor like) devices. From the group of semiconductors, Molybdenum disulfide (MoS₂), a 2D-semiconductor with direct bandgap and one of the transition-metal dichalcogenide with a peculiar layered structure, shows qualities such as high electrical conductivity, stable chemical properties, high electron mobility and a large surface area.^{5,6} Because of its outstanding light absorption in the visible and infrared ranges, MoS₂ has applications in optoelectronics in a wide range. This optical energy absorption characteristic can be attributed to MoS₂'s bandgap of 1.3 to 1.8 eV.⁷ Furthermore, because of the optoelectronic and electrical characteristics of

MoS₂, which are its layer dependent, this gives a straightforward approach to tailor the properties to the application. Despite its amazing characteristics, MoS₂ has certain drawbacks, such as rapid recombination of photogenerated electron-hole pairs and a poor transfer rate of the electron. To mitigate the disadvantages, MoS₂ mixes have been coupled with semiconducting materials to improve the characteristics of MoS₂ and broaden the range of applications.⁸ The excellent ideal qualities of ZnS nano phosphor include a broad direct bandgap (3.72 eV, 3.77 eV for cubic phased ZnS and for hexagonal phased ZnS, respectively), good transport capabilities, and high electron mobility.⁹ It was used in numerous luminescence and optoelectronic applications like LEDs- light-emitting diodes, sensors, photochemical-catalysis, solar cells and biological devices due to its strong photoabsorption capabilities.¹⁰⁻¹² Aside from these intriguing features, it is a suitable material for optoelectronics because of its acceptable stable thermal property and high transmittance in the IR region.¹³ Both ZnS and MoS₂ have similar lattice characteristics and both are sulfur sourced and semiconducting in nature.¹⁴ When compared to separate ZnS and MoS₂ nanomaterials, nanocomposite of ZnS-MoS₂ reflects enhanced optical and structural characteristics.⁸

The partially filled d-orbital enables¹⁵ the transition metal ion Mn²⁺ to exhibit unique fascinating optical, catalytic, electrical, and magnetic characteristics when doped into ZnS-MoS₂ nanocomposites. The hydrothermal approach for producing nanophosphors is a simple and adaptable process that produces nanoparticles with highly regulated size and shape.¹⁶ The current study aims to prepare undoped and Mn²⁺ doped nanocomposites of ZnS-MoS₂ and the influence of Mn²⁺ ions on spectral and structural properties of prepared samples. The prepared samples were synthesized by hydrothermal method and were examined by employing several characterisation methods such as XRD, SEM with EDAX, DRS, and FT-IR spectrum investigations.

EXPERIMENTAL

Materials

All ingredients of 99.9 percent purity were employed to synthesize pure and Mn²⁺ doped ZnS-MoS₂ nanocomposites using hydrothermal technique. As starting materials, sodium molybdate dihydrate (Na₂MoO₄·2H₂O), zinc acetate dihydrate (C₄H₁₀O₆Zn), thiourea (CH₄N₂S), sodium hydroxide (NaOH), and manganese oxide (MnO) were employed. The dilution process and sample synthesis process took place by consuming Double De-ionized water. Acetone was employed for cleaning all the glassware used in this process of preparation.

Composite Preparation

Undoped and MnO doped nanocomposites of ZnS-MoS₂ were synthesized in a stoichiometric ratio utilizing a single-step hydrothermal technique in this approach CH₄N₂S, Na₂MoO₄·2H₂O, Zn(CH₃COO)₂·2H₂O, and MnO were weighed and poured into a 250 ml conical flask containing 100 ml of double de-ionized water. And the chemical assembly was stirred for two hours with the aid of a magnetic stirrer while adding, drop-wise, 0.2 Molar solution of NaOH of volume 10 c.c. After the process of stirring, the thoroughly mixed chemical collection was conveyed into a Teflon-lined autogenous pressured autoclave of volume 150 ml. The autoclave was placed in a controllable temperature hot air oven for a time period of 12 hours at a temperature of 180 °C. After that, the autoclave was allowed to cool to ambient temperature for 12 hours, after which a precipitate in black color developed and was collected. This precipitate which is collected, was centrifuged by operating centrifuge machine at 10,000 r.p.m., and washed 4 times alternatively with ethanol and double-deionized water. The resulting black precipitate was allowed to dehydrate at 120°C for a time span of 6 hours before being ground using an agate mortar. The produced MnO doped nanocomposite of ZnS-MoS₂ was obtained in powder form. The same process is used for undoped samples without the addition of MnO.

In the process of synthesis of ZnS-MoS₂ nanocomposites the following chemical equations are involved.

- (1) For MoS₂; $4\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} + 9\text{CH}_4\text{N}_2\text{S} + 4\text{H}_2\text{O} \rightarrow 4\text{MoS}_2 + \text{Na}_2\text{SO}_4 + 6\text{NaOH} + 9\text{CO}_2 + 18\text{NH}_3$
- (2) For ZnS; $\text{CS}(\text{NH}_2)_2 + \text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} \rightarrow \text{ZnS} + 2\text{CH}_3\text{COONa} + 2\text{NH}_3 + \text{CO}_2 + 2\text{H}_2\text{O}$
- (3) For ZnS-MoS₂; $4\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} + 8\text{NaOH} + 4\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} + 13\text{CS}(\text{NH}_2)_2 + 4\text{H}_2\text{O} \rightarrow 4(\text{ZnS-MoS}_2) + \text{Na}_2\text{SO}_4 + 13\text{CO}_2 + 8\text{CH}_3\text{COONa} + 26\text{NH}_3 + 8\text{H}_2\text{O} + 6\text{NaOH}$

The Chemical Constituents of prepared samples with a variation of MnO are shown below.

Mn₀: 60.0% ZnS + 40% MoS₂

Mn₁: 59.7% ZnS + 40% MoS₂ + 0.3% MnO

Mn₂: 59.4% ZnS + 40% MoS₂ + 0.6% MnO

Mn₃: 59.1% ZnS + 40% MoS₂ + 0.9% MnO

Characterizations and Analytical Tools

At room temperature, the nature (crystalline or amorphous) of the synthesized undoped and Mn²⁺ doped nanocomposites of ZnS-MoS₂ were characterized using tabletop Rigaku-MiniFlex600 model, here Cu-K α radiation with wavelength=1.5406Å was used, and scanned from 3° to 90°. Analytik-Jena-UV-VIS-NIR-SPECORD-210-plus, DRS-spectrophotometer, in width from 200 to 1000nm, was employed to record the spectrum in reflection mode (DRS) of the synthesized sample. By using Jeol JSM IT- 500 models SEM assembled EDAX, the morphology and presence of compositional elements of the prepared nanopowder were carried out. The FT-IR spectrum, from 4000 cm⁻¹ to 400 cm⁻¹, of the hydrothermally prepared sample, was recorded on Bruker ALPHA II model FT-IR instrument using KBr pellet. The luminescence studies were recorded on a Xenon lamp equipped PERKIN ELMER LS-55 spectrometer by exciting the samples at wavelength 337 nm.

RESULTS AND DISCUSSION

Structural and SEM Properties

XRD Study

The XRD pattern recorded related to undoped and Mn²⁺ doped ZnS-MoS₂ nanocomposites is shown in Fig.-1. The pattern is in good accordance with JCPDS Card Numbers: 01-077-2100 and 00-012-0688 related to the cubic ZnS phase and hexagonal phase of ZnS(Wurtzite-10H). The hexagonal MoS₂ phase as its prominent peak appears at 2 θ value 14.02°, which is in good accordance with JCPDS Card Numbers: 01-075-1539.^{7,17,18} The standard JCPDS Patterns related to cubic-ZnS, hexagonal-ZnS and hexagonal-MoS₂ are depicted in Fig.-2. The good crystallization of synthesized samples is confirmed by the strong and narrow peaks from XRD graphs. The hexagonal phase of MoS₂ and dual phases (Cubic and Hexagonal) of ZnS are reflected from the XRD pattern of undoped nanocomposite of ZnS-MoS₂.^{7,17,18}

Due to the increase in concentration Mn²⁺ ions, it is noticed that there is a considerable increase in phase of cubic-ZnS contrast to hexagonal phase of ZnS and lattice related parameters were also changed. The estimated cell parameters are shown in Table-1, which are in well agreement with the values of standard JCPDS cards.

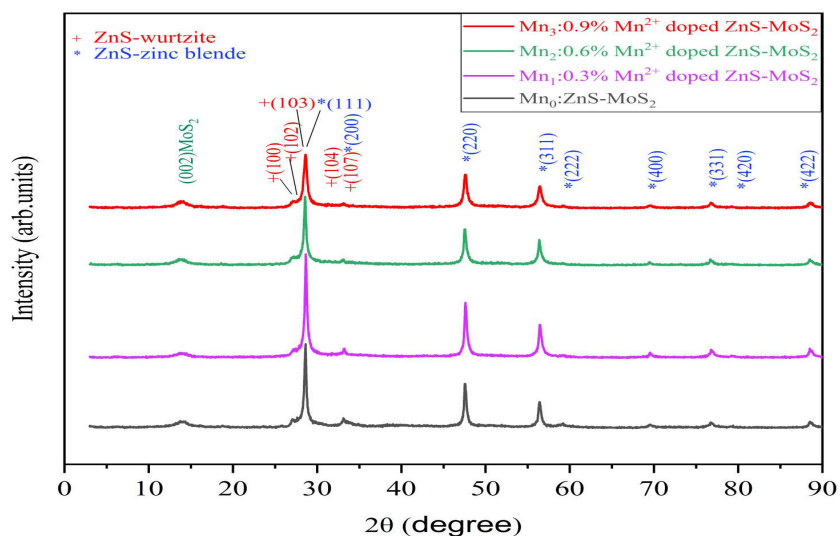


Fig.-1: XRD Pattern of ZnS-MoS₂ and Mn²⁺ doped ZnS-MoS₂ Nanocomposites

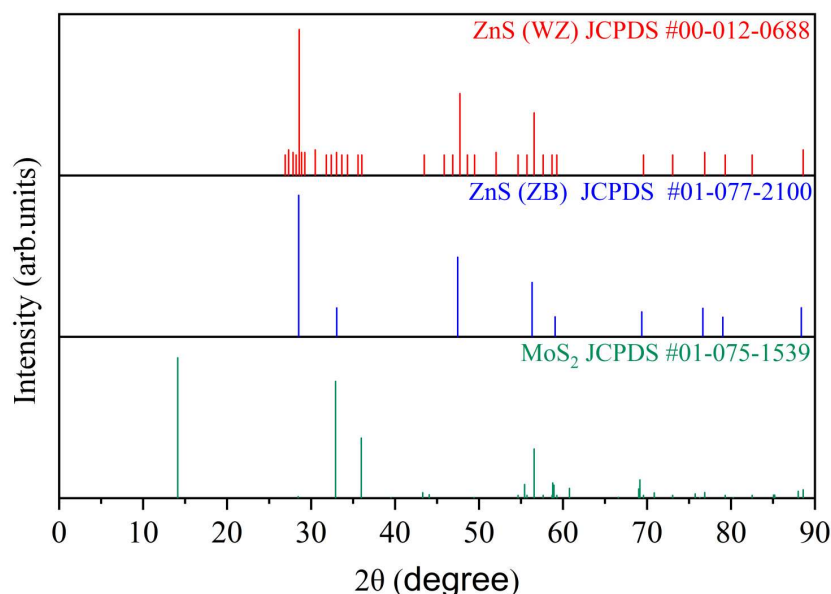


Fig.-2: The JCPDS Standard XRD Pattern of Cubic and Hexagonal ZnS and Hexagonal MoS₂

To estimate crystallite size (D), Debye-Scherrer's formula was used. The formula is as shown below:

$$D = \frac{k\lambda}{(\cos \theta)\beta}$$

Where, k (= 0.9) is shape factor, λ is related to the Cu-K α wavelength (1.5406 Å), β and θ are full width at half maximum (FWHM) and diffraction angle respectively (both are in radians).¹⁹

The values of δ -Dislocation density and ϵ -lattice-strain- ϵ were evaluated using the formulae, $\delta = \frac{1}{D^2}$ and $\epsilon = \frac{\beta}{4\tan\theta}$ respectively.^{20,21} The estimated values of crystallite size, dislocation density and lattice-strain in the prepared sample were obtained and are tabulated in Table-2. Due to the MnO doping, the doped samples showed a decrease in the size of crystallite. The dislocation-density and micro-strain are increased with crystallite size decrement, which is in good accordance with the previous report.²² The dislocation density and micro-strain values are identified to raise with the diminishing size of crystallite as the concentration of dopant ion increases.

Table-1: Calculated Lattice Parameters of prepared Undoped and Mn²⁺ Doped Nanocomposites of ZnS-MoS₂.

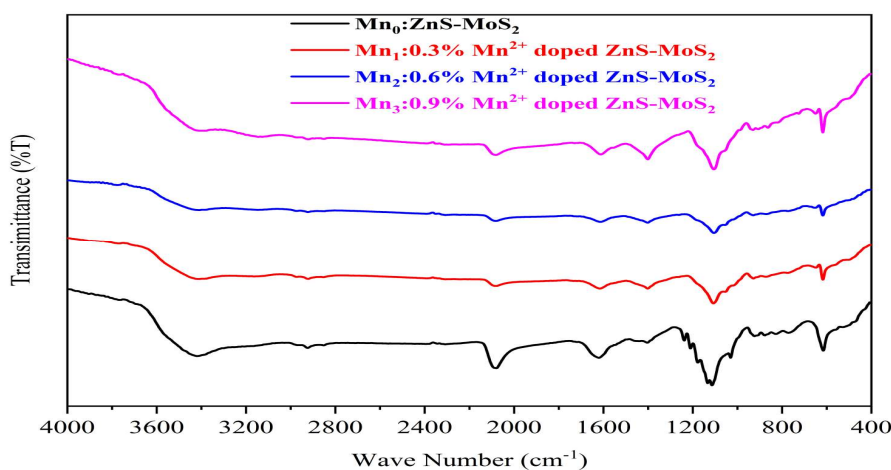
Sample Code	ZnS					MoS ₂		
	Cubic Phase		Hexagonal Phase			Hexagonal Phase		
	Lattice Parameter s (Å)	Volume of Unit Cell (Å ³)	Lattice Parameters (Å)		Volume of Unit Cell (Å ³)	Lattice Parameters (Å)		Volume of Unit Cell (Å ³)
	a=b=c	(a ³)	a=b	c	($\frac{\sqrt{3}}{2}a^2c$)	a=b	c	($\frac{\sqrt{3}}{2}a^2c$)
Mn ₀	5.4060	157.99	3.8400	30.37	387.82	3.1838	12.87	112.97
Mn ₁	5.4050	157.90	3.7960	31.22	389.60	3.1707	12.63	109.96
Mn ₂	5.4060	157.99	3.8210	31.10	393.23	3.1646	12.56	108.93
Mn ₃	5.4070	158.08	3.8200	31.10	393.02	3.1445	12.43	106.44
JCPDSC	#5.4145	#158.74	\$3.8200	\$31.20	\$394.29	@3.1400	@12.53	@106.99
ard No.	#01-077-2100		\$00-065-0688			@01-075-1539		

Table-2: Average Crystallite Size, induced Lattice-strain and Values of Dislocation Density for Undoped and Mn²⁺

Doped ZnS-MoS ₂ Nanocomposites					
Sample-Code	Position (2θ)- (degree)	FWHM-(β)	Crystallite Size - (D) (nm)	Lattice strain- [(ε)×10 ⁻⁴]	Dislocation Density- (δ) (lines/m ²)
Mn ₀	28.60 ⁰	0.4170	19.67	71.39	2.58×10 ¹⁵
Mn ₁	28.66 ⁰	0.4443	18.46	75.89	2.93×10 ¹⁵
Mn ₂	28.56 ⁰	0.4993	16.43	85.59	3.70×10 ¹⁵
Mn ₃	28.60 ⁰	0.6276	13.07	107.89	5.85×10 ¹⁵

FT-IR: Fourier Transform Infrared Spectroscopy

To inspect and confirm the presence of precursor residuals and to inspect the presence of different vibrational modes and characteristic functional groups presented in undoped and Mn²⁺ doped ZnS-MoS₂ nanocomposites FT-IR technique is employed, in the vicinity of 4000 - 400 cm⁻¹, in the transmittance mode and corresponding FT-IR spectra are presented in Fig.-3. The functional groups with the corresponding wavenumber are represented in Table-3. By comparing undoped and Mn²⁺ doped FT-IR spectra's, it is clear that all the samples exhibit the same features, but the position of peaks and intensity of the peaks were little bit changed.

Fig.-3: FT-IR Spectra of Pure and Mn²⁺ doped ZnS-MoS₂ Nanocomposites

A broad dip, because of strong interaction of H₂O with ZnS lattice surface, appears at 3420 cm⁻¹ due to O-H Stretching, this occurs due to the precursor related residuals during the processes of characterization or samples preparation.²³ Due to -CH₂ stretching peaks appearing near 2064-2080 cm⁻¹²⁴ and H-O-H bending mode attributed to the appearance of peaks at around 1620-1637cm⁻¹.²³ The bending vibration mode of H₂O at around 1620- 1637 cm⁻¹ confirms the presence of H₂O.

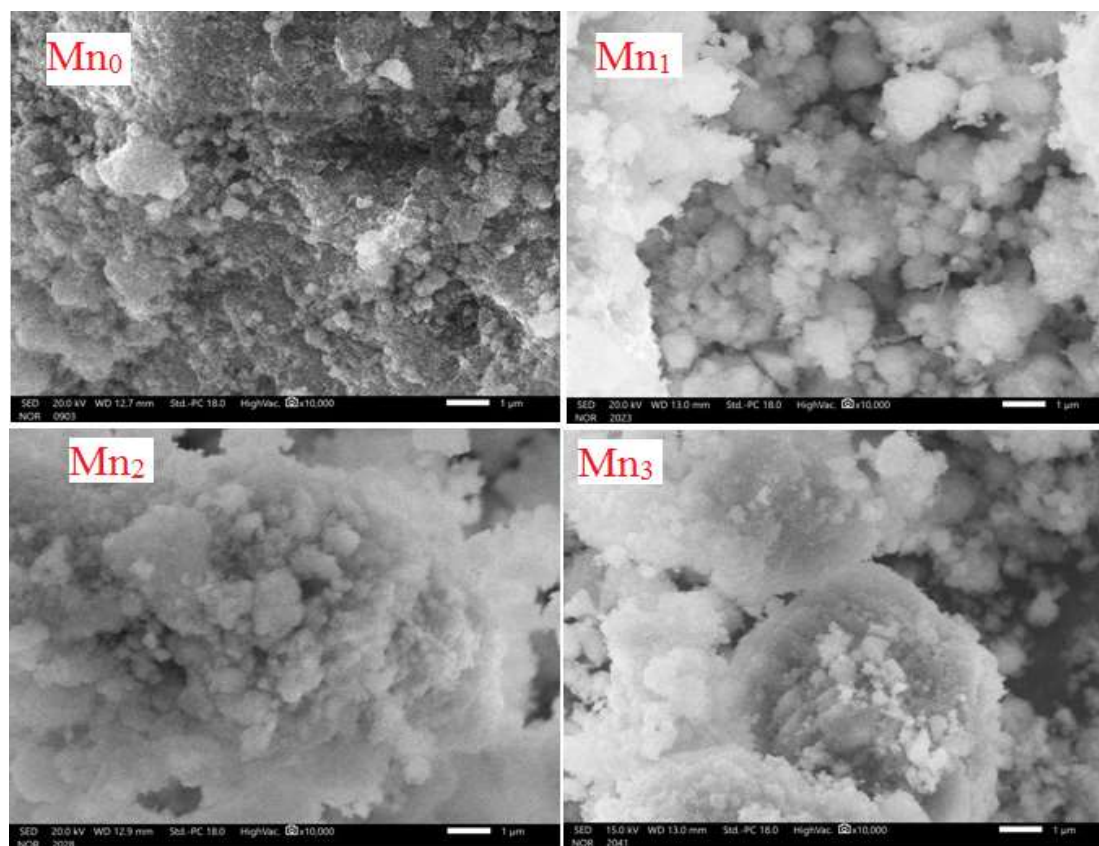
The C-H stretching mode is confirmed due to bands observed near 1404 to 1401 cm⁻¹.²⁵ The complex sulfur formation in MoS₂ was confirmed by the presence of bands located near 1133 cm⁻¹ to 991 cm⁻¹.²⁶ The bands around 924 and 762 cm⁻¹ are ascribed to Zn-S vibrational mode.²⁷ The S-Mo-S vibration bands near 876,863,617 and 616 cm⁻¹ appeared.²⁸

SEM with EDAX Studies

The SEM technique is used to investigate the surface morphology of prepared nanocomposites of ZnS-MoS₂. Fig.-4 shows micrograms of undoped and Mn²⁺ doped nanocomposites. SEM morphological pictures of, without MnO sample reveal spherical ZnS spheres and sheets of MoS₂. As the Mn²⁺ ions doping concentration increases from 3 of 100 mole percent to 9 of 100 mole percent, the inter-atomic distance, which separates spherical shapes, is decreasing, forming a flower liked spherical network on MoS₂ nano-flakes sheet.

Table-3: IR Band Assignment, Intensity with its Relevant Wave Number Region for ZnS-MoS₂ and Mn²⁺ Doped ZnS-MoS₂ Nanocomposites

Vibrational Frequency (cm ⁻¹)				Assignment of Various Bands
Mn ₀	Mn ₁	Mn ₂	Mn ₃	
616	617	618	617	Stretching mode S-Mo-S vibrational bonds
762	-	-	-	Stretching mode Zn-S vibrational bonds
876	-	-	863	S-Mo-S bonds vibrations (Stretching mode)
924	924	925	929	Vibrations of Zn-S
1030	1048	1048	1048	MoS ₂ active sites
1117	1105	1104	1103	MoS ₂ active sites
1404	1399	1398	1398	C-H stretching
1621	1617	1617	1612	H ₂ O molecules on the particle surface
2080	2085	2080	2086	CH ₂ Stretching vibration
3420	3418	3414	3418	bonded and non-bonded Stretching vibration due to –O–H groups

Fig.-4: SEM Micrographs for the ZnS-MoS₂ (Mn₀) and Mn²⁺ Doped ZnS-MoS₂ (Mn₁, Mn₂ and Mn₃) Nanocomposites

The elemental composition of the prepared undoped and Mn²⁺ doped nanocomposites of ZnS-MoS₂ was studied by EDAX energy-dispersive X-ray spectroscopy, and their relevant spectra are depicted in Fig.-5. The elemental compositions of Mo, Zn, S, and Mn that were obtained in practice were shown as an inset table in Fig.-5 for each sample. The results obtained are in good accordance with the stoichiometric calculations performed for this experiment. The compositional analysis reflects that there is a significant increase in the contents of O₂ and Mn and a decrease in the contents of Mo and Zn. This happens may be due to MnO doping. This is a clear indication of replacement of Zn, Mo with Mn²⁺ ions.

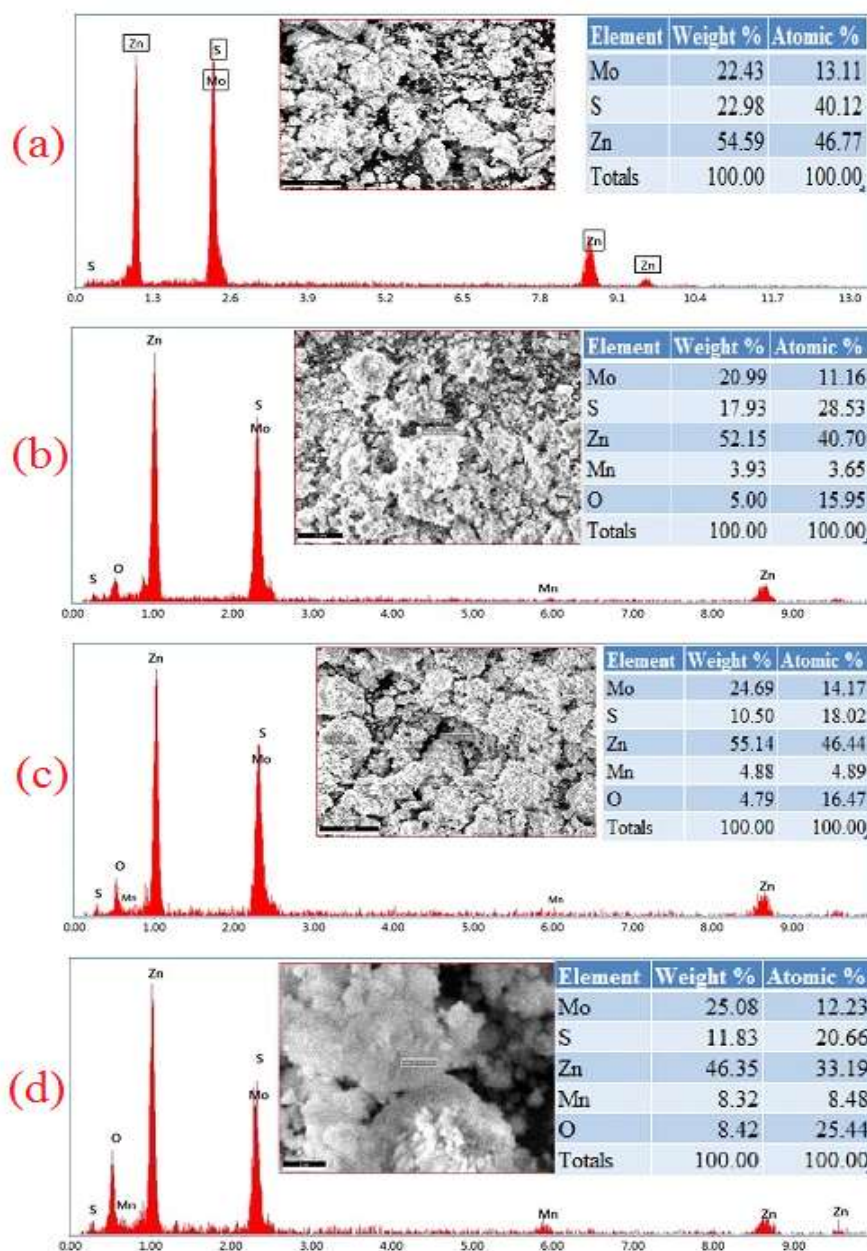


Fig.-5: Images of EDAX Spectra of (a) ZnS-MoS₂ and (b) 0.3 mol%, (c) 0.6 mol% and (d) 0.9 mol% of Mn²⁺ Doped ZnS-MoS₂ Nanocomposites

DRS Studies

DRS is a convenient technique for powdered samples as it doesn't need any appropriate medium to record the spectrum. From the collected data of reflection spectra, in the range from 200 to 1000 nm, the bandgap calculations were performed. The well-known Kubelka-Munk (K-M) relation is used to estimate the band gap values of the prepared MoS₂ nanopowder sample:

$$F(R) = \frac{(1 - R)^2}{2R}$$

Where R is the reflectivity of the powder sample, F(R) denotes K-M function corresponding to absorbance.

The relation connecting band gap (E_g) and coefficient of absorption (α)²⁹, is-

$$(\alpha h\nu) = A (h\nu - E_g)^n$$

This equation can be rearranged as-

$$(\alpha h\nu) = F(R)h\nu = A (h\nu - E_g)^n$$

Where $h\nu$ denotes the energy of an incident photon, 'A' is a constant depending on transition probability, $n = \frac{1}{2}, \frac{3}{2}, 2$ and 3 for direct transition-allowed, direct transition-forbidden, indirect transition-allowed and indirect transition-forbidden, respectively.³⁰

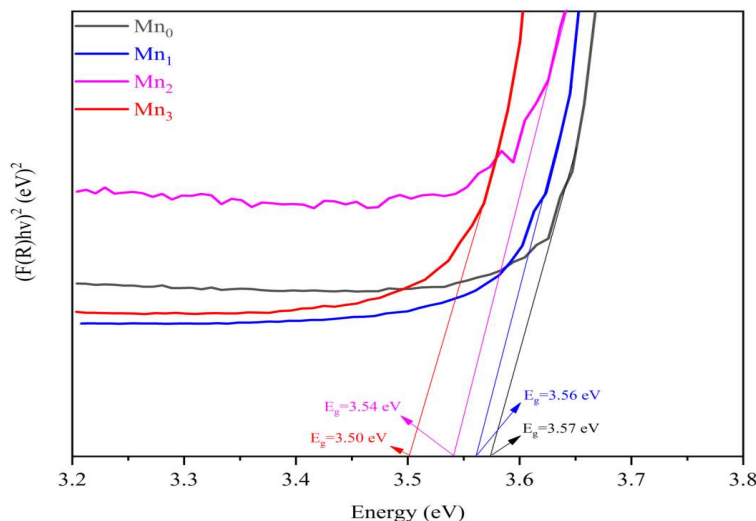


Fig.-6: DR Spectra of Undoped and Mn^{2+} Doped Nanocomposites of ZnS-MoS₂

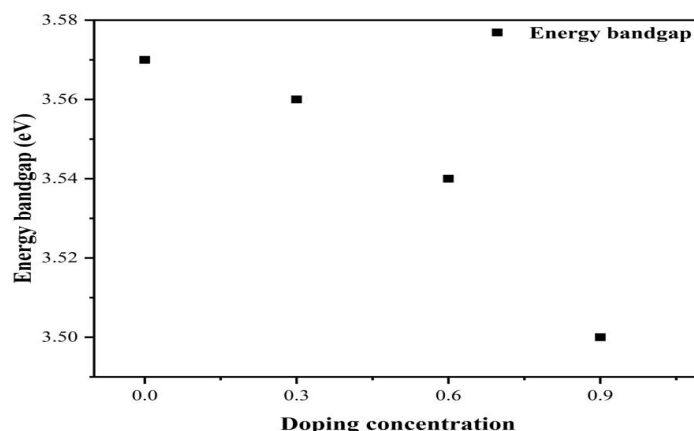
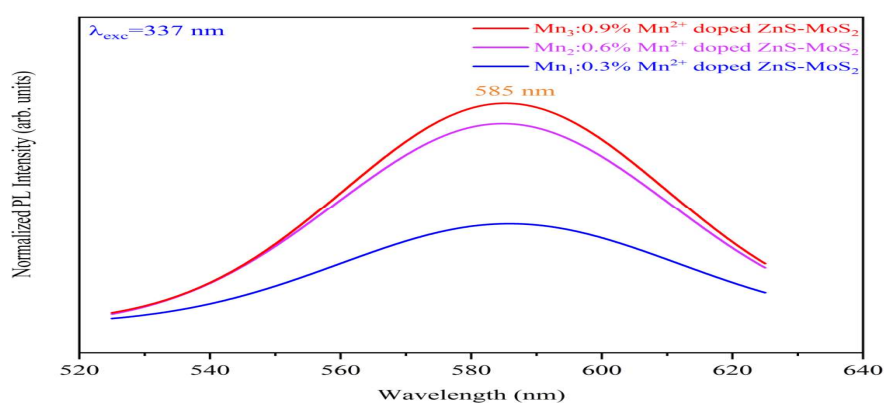
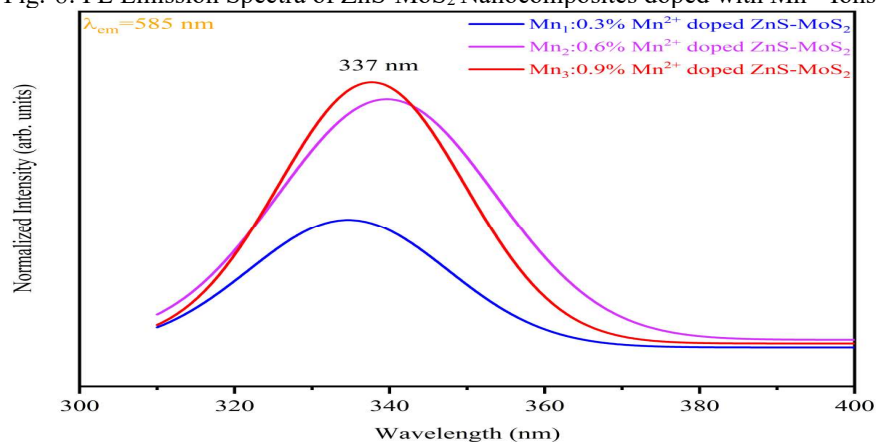
A graph, as shown in Fig.-6, is plotted by taking $(F(R)h\nu)^2$ on y-axis and $h\nu$ on x-axis. From the graph, bandgap values are extrapolated for the Mn^{2+} doped and undoped ZnS-MoS₂ nanocomposites. In the current study, it was discovered that as the doping concentration of Mn^{2+} ions increases, the energy bandgap decreases slightly. This is due to the replacement or interstitial of Mn^{2+} ions in the prepared host lattice, as well as structural deformation occurs in that host lattice, which introduces interface states. The obtained energy bandgap values from 3.57 eV to 3.50 eV are plotted as a graph in Fig.-7, with band gap values tabulated in Table-4. When comparing the reflectance spectra of Mn^{2+} doped with pure ZnS-MoS₂, the reflectance spectra of Mn^{2+} doped samples and pure ZnS-MoS₂ sample show nearer features but are shifted slightly to low frequency regions (red shifted-from band gap value 3.57 to bandgap value 3.50 eV) quantum confinement is revealed here.

Photoluminescence

Photoluminescence (PL) spectroscopy is a perfect tool to characterize the optoelectronic properties of a semiconductor, it provides statistics related to defect states, which involve in radiative de-excitation of the sample. In the visible region, 400-700 nm, the radiative particle room temperature photoluminescence (PL) spectra were collected by exciting at a wavelength of 337 nm and the collected spectra were analyzed to understand the luminescence efficiency.^{31,32} PL emission and excitation spectra of Mn^{2+} doped nanocomposites of ZnS-MoS₂ are depicted in Fig.-8 and Fig.-9 and the corresponding PL emission spectra peaks are tabulated in Table-5.

Table-4: Energy Band Gap Values and their Variation related to Pure and Mn^{2+} Doped Nanocomposites of ZnS-MoS₂

Sample-code	MnO Doping Concentration (mol%)	Bandgap (eV)	Size of Crystallite (nm)
Mn ₀	0	3.57	19.67
Mn ₁	0.3%	3.56	18.46
Mn ₂	0.6%	3.54	16.43
Mn ₃	0.9%	3.50	13.07

Fig.-7: Energy Bandgap Variation with Mn²⁺ Ion Doping ConcentrationFig.-8: PL Emission Spectra of ZnS-MoS₂ Nanocomposites doped with Mn²⁺ IonsFig.-9: PL Excitation Spectra of ZnS-MoS₂ Nanocomposites doped with Mn²⁺ Ions

All the Mn²⁺ ions doped samples exhibit visible range emission peaks around 585 nm. Thus the visible range of Photo-Luminescence emission spectra peaks can be directly connected to the internal defect density of a nanomaterial. The intensity of Photo Luminescence emission is identified to increase as the doping concentration of MnO increases. With the effect of Mn²⁺ dopant ions in the ZnS-MoS₂ host, lattice emission peaks are observed around 585 nm and show quantum confinement. The exciton (or) band edge emission occurs due to the conduction electron of host lattice being trapped by deep trap centers or surface states; when the manganese exists in the host lattice the energy of these trapped electrons transferred to doped ions through exchange interaction process. This internal emission mechanism indicates the Mn²⁺ ions influence on the luminescence behavior.³³⁻³⁵

Table-5: Peak Position Shifting in PL Spectra with Mn^{2+} Ion Concentration related to Mn^{2+} doped ZnS-MoS_2 Nanocomposites

Sample Code	Mn^{2+} Concentration	Position of Peak in PL Spectrum I(λ nm)
Mn_1	0.3%	585
Mn_2	0.6%	585
Mn_3	0.9%	585

The characteristic luminescence peak at 585 nm in yellow-orange region is related to spin forbidden transition ${}^4\text{T}_1({}^4\text{G}) \rightarrow {}^6\text{A}_1({}^6\text{S})$ of Mn^{2+} ions.^{34,36} After excitation, transfer of excitation energy takes place from the conduction band of ZnS-MoS_2 host to the excited charge carriers. Previous reports suggest that when Mn^{2+} ion is doped into host lattice, it can occupy distinct host lattice sites.³⁷⁻³⁹ The wavelength of PL emission depends upon the Mn^{2+} ions distribution in the host lattice. The PL emission has slightly different wavelengths 557, 578, 585, 600 and 635 nm when Mn^{2+} ions are located in the tetrahedral cubic lattice, near the point defect, incorporated into the ZnS lattice, in the octahedral interstices and exists MnS form in ZnS , respectively.^{37, 40-44} Therefore, the nature of the distribution of dopant (Mn^{2+} ions) in the host lattice decides the particular peak position in the Photo Luminescence emission spectra. In PL emission spectra, an emission band near 585 nm (${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$) was noticed from all the Mn^{2+} doped samples in the present case. This supporting result energetically suggests that the dopant ions were successfully incorporated into the ZnS-MoS_2 lattice. Hence, the photoluminescence bands can be connected with transitions involving donors, acceptors and surface states^{33, 34}. The high photoluminescence intensities obtained from the Mn^{2+} doped of ZnS-MoS_2 nanocomposites highlight their importance in future optoelectronic and photonic device applications.⁴⁵⁻⁴⁷

CONCLUSION

The hydrothermal route was used to successfully prepare Mn^{2+} doped and undoped ZnS-MoS_2 nanocomposites. Mn^{2+} doped nanocomposites showed cubic- ZnS -phase, hexagonal- ZnS -phase and hexagonal phase of MoS_2 in XRD spectra. There is a lattice distortion caused by Mn^{2+} ions occupied in the host lattice, which causes a decrease in the hexagonal- ZnS -phase proportion compared to the cubic- ZnS -phase without disturbing the MoS_2 -hexagonal-phase. The calculated average crystallite sizes of hydrothermally prepared nanocomposites are in the order of 12nm - 20nm and moreover calculated the dislocation density and micro-strain to better understand the samples' internal distortion. The FT-IR spectrum was used to examine the molecular vibrations and different functional groups present in the prepared samples. SEM studies of the prepared samples confirm the morphology of ZnS spheres on the hexagonal flower-like MoS_2 flakes. With the increase in doping of Mn^{2+} , the separation between the hexagonal spheres is decreased. The presence of various elements in the samples is confirmed by EDAX results based on stoichiometry. The results of DRS spectra confirm that the optical energy band gap decreases as the concentration of Mn^{2+} doping in the host lattice increases, indicating quantum confinement of synthesized samples. Photoluminescence results show yellow-orange light emission, which is due to the dopant, Mn^{2+} ions, incorporated in the ZnS-MoS_2 host, further due to d-d (${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$) transition and with the influence of Mn^{2+} ions exhibiting single peak at 585 nm under Visible light region. The intense PL emission properties of MnO doped ZnS-MoS_2 nanocomposite samples specifies the efficient and fruitful utilization of these materials in future optoelectronic and photonic device applications.

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REFERENCES

1. A. D. Yoffe, *Advances in Physics*, **51**, 799(2002), <https://doi.org/10.1080/00018730110117451>
2. F. Wang, Q. Li and D. Xu, *Advanced Energy Materials*, **7**, 1700529(2017), <https://doi.org/10.1002/aenm.201700529>

3. P. H. Camargo, S. Cury, K. Gundappa and F. Wypych, *Materials Research*, **12**, 1(2009), <https://doi.org/10.1590/S1516-14392009000100002>
4. S. Ouendadji, S. Ghemid, H. Meradji and F. E. H. Hassan, *Computational Materials Science*, **50**, 1460(2011), <https://doi.org/10.1016/j.commatsci.2010.11.035>
5. C. Li, J. Li, Z. Wang, S. Zhang, G. Wei, J. Zhang, H. Wang and C. An, *Inorganic Chemistry Frontiers*, **4**, 309(2017), <https://doi.org/10.1039/C6QI00502K>
6. S. Qin, W. Lei, D. Liu and Y. Chen, *Scientific Reports*, **4**, 7582(2014), <https://doi.org/10.1038/srep07582>
7. L. Wang, J. Jie, Z. Shao, Q. Zhang, X. Zhang, Y. Wang, Z. Sun and S.-T. Lee, *Advanced Functional Materials*, **25**, 2910(2015), <https://doi.org/10.1002/adfm.201500216>
8. S. V. P. Vattikuti, C. Byon and S. Jeon, *Physica B: Condensed Matter*, **502**, 103(2016), <https://doi.org/10.1016/j.physb.2016.08.050>
9. X. Fang, L. Wu and L. Hu, *Advanced Materials*, **23**, 585(2011), <https://doi.org/10.1002/adma.201003624>
10. X. S. Fang, C. H. Ye, L. D. Zhang, Y. H. Wang and Y. C. Wu, *Advanced Functional Materials*, **15**, 63(2005), <https://doi.org/10.1002/adfm.200305008>
11. P. T. Gomathi, P. Sahatiya and S. Badhulika, *Advanced Functional Materials*, **27**, 1701611(2017), <https://doi.org/10.1002/adfm.201701611>
12. L. Hu, M. M. Brewster, X. Xu, C. Tang, S. Gradečak and X. Fang, *Nano Letters*, **13**, 1941(2013), <https://doi.org/10.1021/nl3046552>
13. S. Hussain, T. Liu, M. S. Javed, N. Aslam and W. Zeng, *Sensors and Actuators B: Chemical*, **239**, 1243(2017), <https://doi.org/10.1016/j.snb.2016.09.128>
14. R. M. Clark, B. J. Carey, T. Daeneke, P. Atkin, M. Bhaskaran, K. Latham, I. S. Cole and K. Kalantar-zadeh, *Nanoscale*, **7**, 16763(2015), <https://doi.org/10.1039/C5NR04790K>
15. E. Sotelo-Gonzalez, L. Rocas, S. Garcia-Granda, M. T. Fernandez-Arguelles, J. M. Costa-Fernandez and A. Sanz-Medel, *Nanoscale*, **5**, 9156(2013), <https://doi.org/10.1039/C3NR02422A>
16. M. R. Abhilash, A. Gangadhar, J. Krishnegowda, M. Chikkamadaiah and S. Srikantaswamy, *RSC Advances*, **9**, 25158(2019), <https://doi.org/10.1039/C9RA04978A>
17. M. R. Saber, G. Khabiri, A. A. Maarouf, M. Ulbricht and A. S. G. Khalil, *RSC Advances*, **8**, 26364(2018), <https://doi.org/10.1039/C8RA05387A>
18. J. Zheng, R. Zhang, X. Wang and P. Yu, *Journal of Materials Science*, **54**, 13509(2019), <https://doi.org/10.1007/s10853-019-03860-7>
19. S. Munimasthani, S. Sarathkumar, U. S. Udaychandran Thampy and R. V. S. S. N. Ravikumar, *Applied Physics A*, **126**, 2(2019), <https://doi.org/10.1007/s00339-019-3180-x>
20. R. Joyce Stella, G. Thirumala Rao, V. Pushpa Manjari, B. Babu, C. Rama Krishna and R. V. S. S. N. Ravikumar, *Journal of Alloys and Compounds*, **628**, 39(2015), <https://doi.org/10.1016/j.jallcom.2014.11.201>
21. S. K. K. Muswareen and S. Cole, *Rasayan Journal of Chemistry*, **13**, 1030(2020), <https://doi.org/10.31788/rjc.2020.1325684>
22. V. D. Mote, Y. Purushotham and B. N. Dole, *Cerâmica*, **59**, 395(2013), <https://doi.org/10.1590/S0366-69132013000300008>
23. D. Ayodhya and G. Veerabhadram, *Journal of Science: Advanced Materials and Devices*, **4**, 381(2019), <https://doi.org/10.1016/j.jsamd.2019.08.006>
24. R. Mendelsohn, C. R. Flach and D. J. Moore, *Biochimica et Biophysica Acta, Biomembranes*, **1758**, 923(2006), <https://doi.org/10.1016/j.bbamem.2006.04.009>
25. S. Mohanapriya, Vennila, M. Kowsalya, S., *Asian Journal of Applied Chemistry Research*, **5**, 26(2020), <https://doi.org/10.9734/ajacr/2020/v5i130125>
26. D. Zhao, T. Wu and Y. Zhou, *Chemistry-A European Journal*, **25**, 9710(2019), <https://doi.org/10.1002/chem.201901715>
27. X. Tian, J. Wen, S. Wang, J. Hu, J. Li and H. Peng, *Materials Research Bulletin*, **77**, 279(2016), <https://doi.org/10.1016/j.materresbull.2016.01.046>

28. M. Yi and C. Zhang, *RSC Advances*, **8**, 9564(2018), <https://doi.org/10.1039/C7RA12897E>
29. S. K. K. Muswareen, M. S. Rao, G. Sridevi and S. Cole, *Materials Science in Semiconductor Processing*, **102**, 104588(2019), <https://doi.org/10.1016/j.mssp.2019.104588>
30. H. Ali and E. S. Mansor, *Colloid and Interface Science Communications*, **39**, 100330(2020), <https://doi.org/10.1016/j.colcom.2020.100330>
31. S. Das Adhikari, A. K. Guria and N. Pradhan, *The Journal of Physical Chemistry Letters*, **10**, 2250(2019), <https://doi.org/10.1021/acs.jpclett.9b00182>
32. R. Viswanatha, S. Sapra, B. Satpati, P. V. Satyam, B. N. Dev and D. D. Sarma, *Journal of Materials Chemistry*, **14**, 661(2004), <https://doi.org/10.1039/B310404D>
33. M. Kawano, H. Takebe and M. Kuwabara, *Optical Materials*, **32**, 277(2009), <https://doi.org/10.1016/j.optmat.2009.08.001>
34. L. Kumari and A. K. Kar, *Dalton Transactions*, **49**, 16979(2020), <https://doi.org/10.1039/D0DT03387A>
35. U. Jabeen, T. Adhikari, S. M. Shah, J.-M. Nunzi, A. Badshah and I. Ahmad, *European Physical Journal Applied Physics*, **78**,(2017), <https://doi.org/10.1051/epjap/2017170102>
36. Y. Gao, Y. Cheng, F. Huang, H. Lin, J. Xu and Y. Wang, *Journal of Alloys and Compounds*, **735**, 1546(2018), <https://doi.org/10.1016/j.jallcom.2017.11.243>
37. J. Cao, J. Yang, Y. Zhang, L. Yang, D. Wang, M. Wei, Y. Wang, Y. Liu, M. Gao and X. Liu, *Journal of Physics D: Applied Physics*, **43**, 075403(2010), <https://doi.org/10.1088/0022-3727/43/7/075403>
38. K. Sooklal, B. S. Cullum, S. M. Angel and C. J. Murphy, *The Journal of Physical Chemistry*, **100**, 4551(1996), <https://doi.org/10.1021/jp952377a>
39. Y. Ohba, M. Mizuta and H. Kukimoto, *Journal of Luminescence*, **28**, 111(1983), [https://doi.org/10.1016/0022-2313\(83\)90029-7](https://doi.org/10.1016/0022-2313(83)90029-7)
40. Y. Y. Bacherikov, N. V. Kitsyuk, T. E. Konstantinova and A. S. Doroshkevich, *Journal of Applied Spectroscopy*, **74**, 408(2007), <https://doi.org/10.1007/s10812-007-0067-y>
41. M. Marandi, G. Hajisalem, N. Taghavinia and M. Houshiar, *Journal of Luminescence*, **131**, 721(2011), <https://doi.org/10.1016/j.jlumin.2010.11.025>
42. R. M. Krsmanović Whiffen, D. J. Jovanović, Ž. Antić, B. Bártová, D. Milivojević, M. D. Dramićanin and M. G. Brik, *Journal of Luminescence*, **146**, 133(2014), <https://doi.org/10.1016/j.jlumin.2013.09.032>
43. P. Sajan, R. Vinod and M. J. Bushiri, *Journal of Luminescence*, **158**, 110(2015), <https://doi.org/10.1016/j.jlumin.2014.09.041>
44. R. Viswanath, H. S. Bhojya Naik, G. S. Yashavanth Kumar, P. N. Prashanth Kumar, K. N. Harish, M. C. Prabhakara and R. Praveen, *Applied Surface Science*, **301**, 126(2014), <https://doi.org/10.1016/j.apsusc.2014.02.013>
45. B. Pejjai, V. R. Minnam Reddy, K. Seku, T. R. R. Kotte and C. Park, *Optik*, **130**, 608(2017), <https://doi.org/10.1016/j.jileo.2016.10.083>
46. T. P. Nguyen, T. B. Vu and Q. V. Lam, *Optical Materials*, **110**, 110537(2020), <https://doi.org/10.1016/j.optmat.2020.110537>
47. A. K. Kole, C. S. Tiwary and P. Kumbhakar, *Journal of Applied Physics*, **113**, 114308(2013), <https://doi.org/10.1063/1.4795779>

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