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Vasyl Stefanyk Precarpathian
National University

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T. Kiran[1], H.M. Parveez Ahmed[2], Noor Shahina Begum[3], Karthik Kannan[4], D. Radhika[5]

Structural, Morphological and Optical Studies of Sol-Gel Engineered Sm^{3+} Activated ZnO Thin Films for Photocatalytic Applications

[1]*SJB Institute of Technology, Bengaluru, Karnataka, India, t.kiran0419@gmail.com*
[2]*Ghousia College of Engineering, Ramanagara, Karnataka, India, parru63@gmail.com*
[3]*Bengaluru University, Karnataka, India, noorsb@rediffmail.com*
[4]*Center for Advanced Materials, Qatar University, P.O Box 2713, Doha, Qatar, karthikkannanphotochem@gmail.com*
[5]*Faculty of Engineering and Technology, Jain-Deemed to be University, Karnataka, India, radhikadv8@gmail.com*

Rare earth (RE) ions activated ZnO thin films were prepared via sol-gel route and the thin films be categorized by various techniques. X-ray diffraction (XRD) studies display the hexagonal wurtzite structure of the prepared thin films. Scherrer's formula was utilized to calculate the average crystallite size (25 - 40 nm) with different Sm^{3+} concentrations. The optical energy gap was calculated by Diffused Reflectance spectra (DRS). The Acid Red (AR) dye was degraded under ultraviolet (UV) light irradiation with ZnO: Sm^{3+}(1-9 mol %) nanostructured thin films and the highest photodegradation (95 %) was observed for 7 mol % of Sm^{3+} doped ZnO catalyst. All the obtained results suggest that prepared material could be a prominent material as photocatalyst.

Keywords: ZnO:Sm^{3+}; thin films; XRD; DRS; photocatalysis.

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Introduction

Materials at nanoscale with various varieties (nanopowder, nano-rods, nano thin films, nano-tubes, nano-flower and nano-wires) find many applications in various fields owing to their novel properties like surface tailoring ability, improved solubility, etc. [1-6]. From the last two decades researchers showing their attention towards the nano-sized metal oxide based semiconductors owing to their attractive properties and potential applications [7].

Among the metal oxide based semiconductors, ZnO has set up a wide variety of applications in CO_2 reduction, water splitting, solar cells, sensors, photocatalysis, telecommunication, etc. owing to its chemical stability, low toxicity and large energy gap of 3.2 eV [8-13].

In particular, ZnO is used as a catalyst for photocatalytic decolorization of organic pollutants due to their rich catalytic efficiency and non-toxic end products [14]. With the evolution of ink, fabric, paint, and paper industries, a large amount of pollutants containing organic dyes are released, which is dangerous to nature. Thus a suitable and economic route (photoreduction, photocatalytic) is very much required to decrease the number of pollutants before releasing into the water environment. It was observed that many researchers doped rare earth ions into the host lattice to enhance catalytic activities. Among rare earth (RE) ions, Sm^{3+} used as a suitable activator which shows intense luminescence, thin bands in visible and UV spectrum due to f orbital transitions which do not interact with the ligand orbitals [15-16].

In the present study, we prepared Sm^{3+} (1-9 mol %) activated ZnO nanostructured thin films by the sol-gel route. Structural, optical and photocatalytic studies of ZnO:Sm^{3+}(1 - 9 mol %) nanostructured thin films were investigated and discussed in detail.

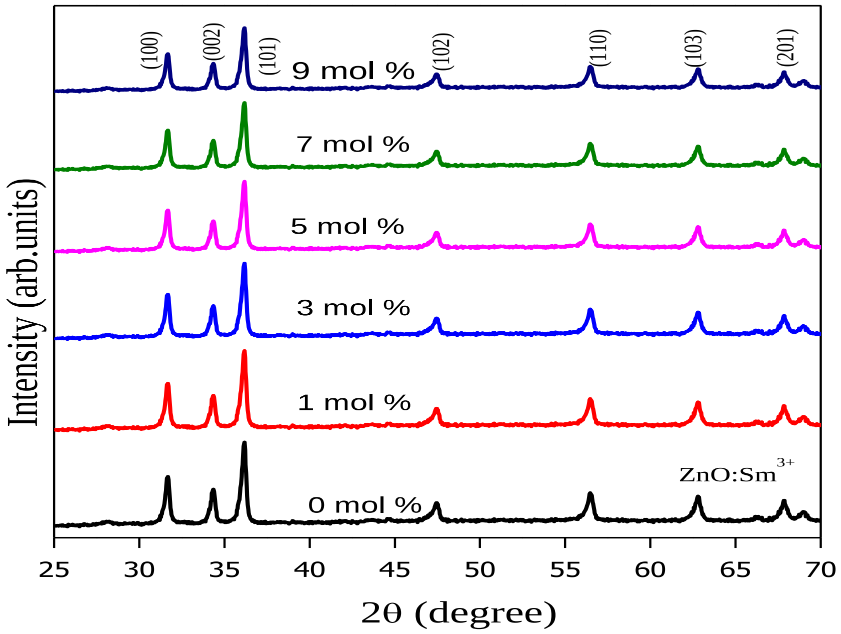

Fig. 1. X-Ray diffraction patterns of ZnO:Sm^{3+}(1-9 mol %) thin films.

I. Experimental

A series of Sm^{3+} activated ZnO thin films were synthesized on glass substrate via sol-gel technique by using analytical grade with 99 % purity of Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) (used as a precursor), Sodium hydroxide (NaOH), Ethanol (CH_2COOH) (reagent), Samarium (Sm_2O_3) and distilled water (solvent medium). In this method stoichiometric amount of Sodium hydroxide and Zinc acetate dihydrate dissolved in the suitable capacity of distilled water in separate beakers and well stirred with a duration of 5 mins then both solutions were poured to the beaker, then ethanol and dopant were added to dropwise, then the solution was accumulated on substrate glass via the deep coating route with 20 mm/min of withdrawal speed, then thin films were dried out by keeping in oven with a temperature of about 200 ºC for 2 hrs further followed by Calcination at 500 ºC for 1 h to eliminate the organic compounds commencing the thin films.

II. Catalytic studies

Photocatalytic experimental studies were carried for the decolourisation of AR dye by taking 250 ml dye solution of 20 ppm and 60 mg of prepared catalyst were seized in an oblique glass beaker (surface area of 176.6 cm^2) under UV light (mercury lamp) source and irradiation were drifting out by concentrating UV light into the combination for 105 mins. Further, the reaction mixture of ~ 5 ml was taken out in an equal interval of times (~15 min) to evaluate the degradation rate of the prepared material.

III. Results and discussion

Fig. 1 indicates the XRD results of pure and 1 - 9 mol % Sm^{3+} doped ZnO thin films prepared by the sol-gel method. All the obtained peaks at (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2) and (2 0 1) were well indexed with the [JCPDS Card No. 36 - 1451] and confirm the hexagonal wurtzite structure of the prepared sample [17]. Also, it was noticed that no other peaks (impurity) were observed in the XRD profile indicates the purity of the sample and sharp peaks confirms the crystallinity of the material. Further, Debye–Scherrer's equation and W-H method were employed (Fig. 2) to find the average crystallite dimension of the material, and relation is expressed in Equation 1 & 2. [18, 19].

$$d = \frac{K\lambda}{\beta cos\theta} \quad (1)$$

$$\beta\cos\theta = \frac{0.9\lambda}{D} + 4\varepsilon\sin\theta \,, \quad (2)$$

where, K defines constant, λ gives wavelength of X-ray, β means full width half maximum and ε: strain, equation 2 plots straight line between '4sinθ' and 'βcosθ' (Fig. 1), the gradient of the line plotted represents the strain and the intercept on the y-axis represents the dimension of the crystallite (D), dislocation density and σ_{stress} were calculated using the following equations 3 & 4, and all the estimated results are described in Table 1.

$$\delta = \frac{1}{D^2} \quad (3)$$

$$\sigma_{stress} = \varepsilon E \quad (4)$$

Further, unit cell volume and lattice parameters were calculated for the plane (1 0 1) using the following

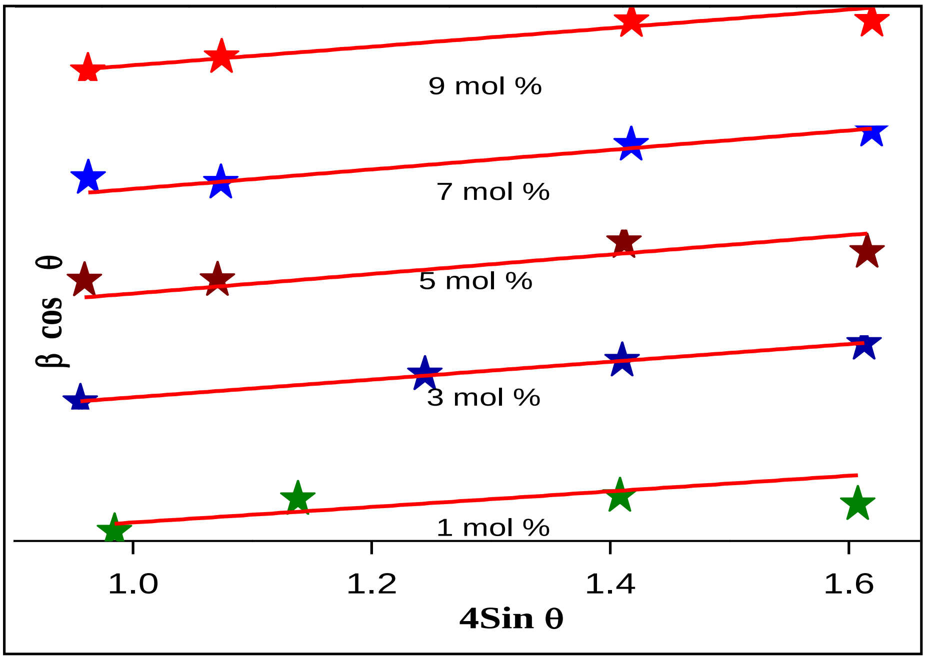

Fig. 2. W-H pattern of ZnO:Sm^{3+}(1-9 mol %) thin films.

Table 1

Lattice parameters of Sm^{3+}(1- 9 mol %) doped ZnO samples

ZnO:Sm^{3+}	Crystallite Size (nm) Scherrer's	Dislocation density δ (lines/m^2) 10^{-3}	Micro-strain ε (10^{-3})	Crystallite Size (nm) W-H plot
0 mol %	26	1.47	1.12	23
1 mol %	30	1.11	1.10	25
3mol %	32	0.97	1.08	26
5 mol %	33	0.91	1.09	29
7 mol %	34	0.86	1.02	30
9 mol %	36	0.77	1.0	33

relations was found to be 51 $Å^3$ and a = b = 3.255 Å, c = 5.2016 Å, respectively.

The addition of dopant ions did not alter the crystalline nature of the material. However, slight modifications in the lattice parameters were observed which is owing to the dissimilarity in the ionic radius between the Sm^{3+} and the host. Peak intensity decreases with the addition of dopant concentration was noticed which is owing to the local symmetry breakdown [18].

Morphology of the surface and shape of the arranged materials were examined by Field Effective Scanning Electron Microscopic technique (FESEM) and the obtained FESEM pictures illustrated in Fig. 3. FESEM images illustrate the nanospirals, nanorings, spherical-shaped morphology, small voids with well-defined boundaries; also rod- shaped morphology were noticed.

Optical studies of pure and doped ZnO thin films was characterized by UV–visible diffused reflectance spectroscopy, obtained results are depicted in Fig. 4 and the DRS spectra show low absorption wavelength at 374 nm indicates the good optical quality of prepared materials which is owing to large exciton binding energy.

The optical bandgap of ZnO and ZnO:Sm^{3+} thin films (Fig. 5) was calculated by using well-known Kubelka-Munk function F(R), and relation is [20].

$$F(R) = \frac{(1-R)^2}{2R}, \qquad (5)$$

where, R represents the percentage of reflectance, by extrapolating the linear part of the curve to intercept the axis of energy, bandgap of ZnO and ZnO:Sm^{3+} was estimated. It was observed that the absorption band shifted to lower energies, band gap energy decreases from 3.2to 3.15eV with raise of dopant concentration which may be due to spin-exchange interaction (sp-d).

Fig. 6 indicates the UV-Vis spectra of the AR dye in the existence of Sm^{3+} activated ZnO thin films under various illumination times of UV light.

It was noted that the absorption peak of AR dye decreases, indicates the deterioration of AR molecules

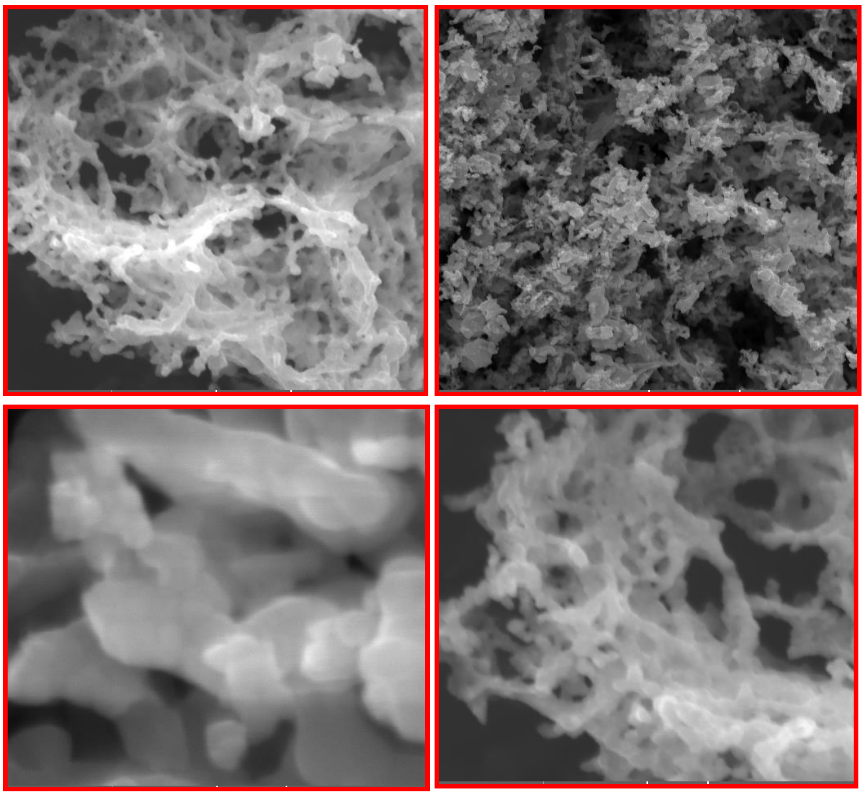

Fig. 3. FESEM images of ZnO:Sm^{3+}thin films.

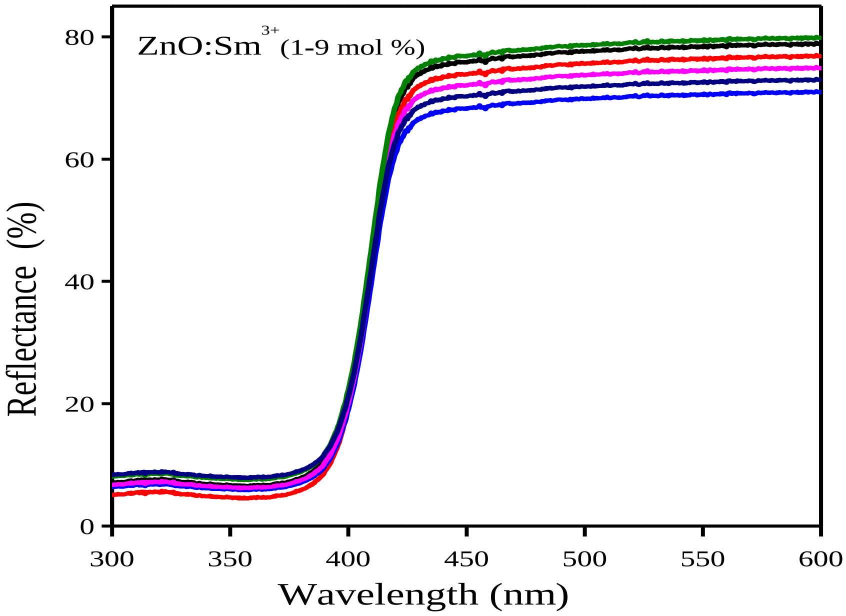

Fig. 4. DRS spectra of ZnO:Sm^{3+}(1-9 mol %) thin films.

under UV light irradiation. Further, insignificant degradation of AR dye was observed in dark conditions and in the absence of ZnO which confirms that degradation of AR dye is due to the presence of photoexcited Sm^{3+} activated ZnO samples. The trend of AR degradation with the presence of prepared 1 - 9 mol % of Sm^{3+} activated ZnO thin films under UV light irradiation are given in Fig. 7 and 95 % of AR dyes were degraded during 105 min. The photocatalyst activity of ZnO: Sm^{3+} samples are rated in the form of 7 mol % ZnO:Sm^{3+} > 5 mol% ZnO :Sm^{3+} > 3 mol % ZnO:Sm^{3+} > 9 mol % ZnO:Sm^{3+} > 1 mol % ZnO:Sm^{3+}.

Langmuir-Hinshelwood kinetics model was used to degradation of AR dye and its kinetics are represented as ln (C/Co) = −kt, Where k be the rate of constant apparent reaction, C be the AR initial concentration, t be the reaction time and C_o be the concentration of AR dye with t, and the obtained kinetics values prepared material is

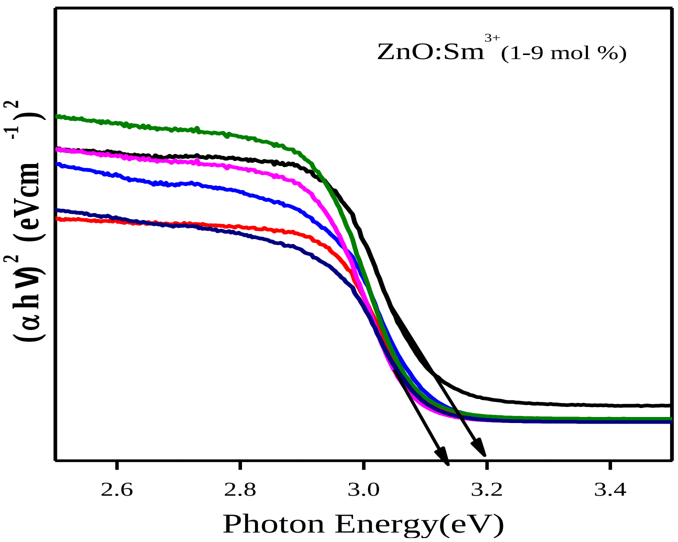

Fig. 5. Bandgap spectra of ZnO:Sm^{3+}(1-9 mol %) thin films.

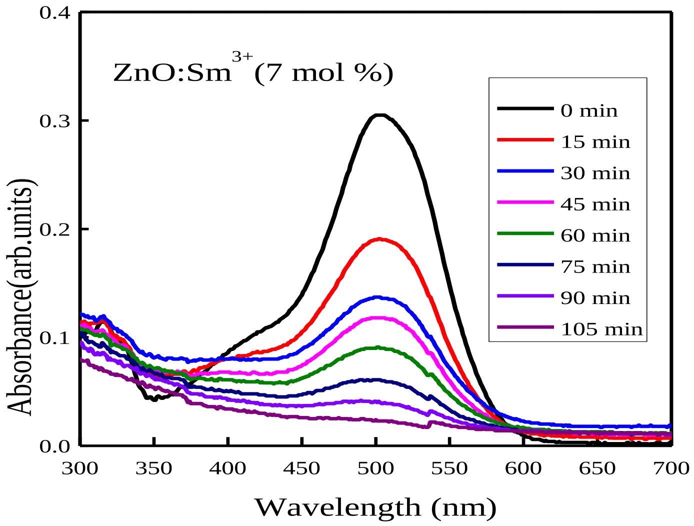

Fig. 6. Absorbance spectra of ZnO:Sm^{3+}(7 mol %) Photocatalysts.

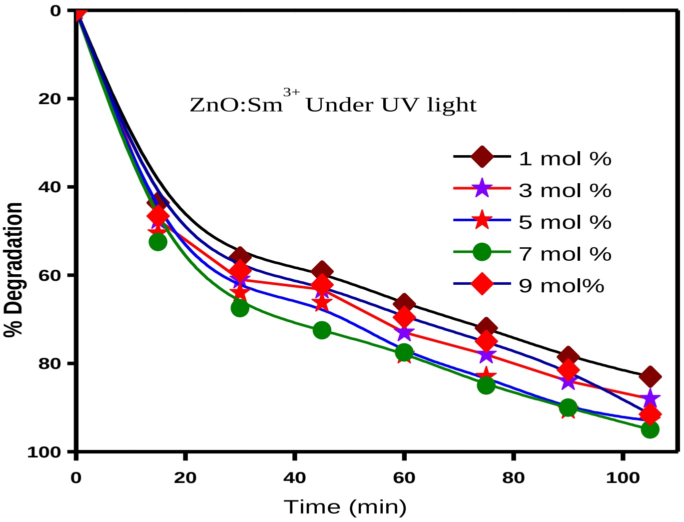

Fig. 7. Plot of % degradation of AR dye under UV light.

Table 2

Kinetics studies on Sm^{3+}(1 - 9 mol %) doped ZnO thin films under UV light illumination

Photocatalysts	% D	K × 10^{-3} min^{-1}
ZnO:Sm^{3+} (1 mol %)	83	23
ZnO:Sm^{3+} (3 mol %)	92	27
ZnO:Sm^{3+} (5 mol %)	93	28
ZnO:Sm^{3+} (7 mol %)	95	29
ZnO:Sm^{3+} (9 mol %)	91.5	26

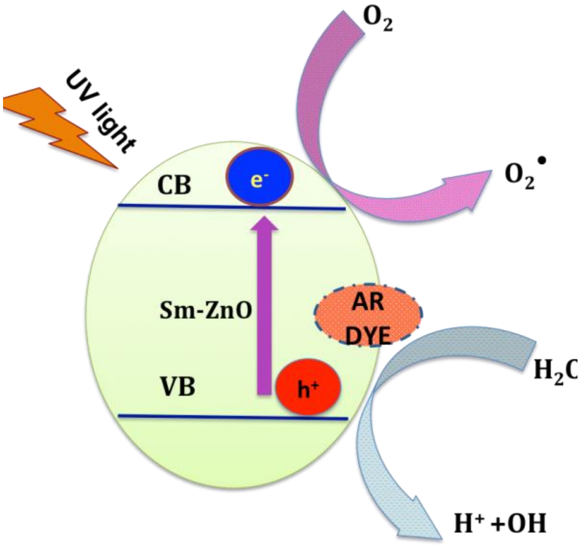

Fig. 8. Schematic representation of photocatalytic activity.

given in Table 2 [21-25].

The improved catalytic activity was noted for 7 mol % doped ZnO:Sm^{3+} catalyst under UV light was observed due to charges carried while separation, which is attributed to the overload production of absorption band shift and radicals hydroxyl to higher wavelengths. Many researchers reported that catalytic performances of the prepared material are based on the factors such as crystallite size, morphologies, textures and the dopant concentration [26-30]. Among, the morphologies of the material and activator concentration played a key role in the photocatalytic activities [30].

General mechanism for photocatalytic process was displayed in Fig 8. This explained the schematic view of AR dye performance in the presence of UV light.

Addition precise quantity of sm^{3+} cations leads to the production of defects which act as trap centres, results in an elevated barrier surface, and region of narrower space charge; however disproportionate quantity of sm^{3+} in the catalyst may lead to the creation of defects, act as the recombination centres which decrease the catalytic efficiency. In the present study, ZnO:Sm^{3+} thin films performs higher ration of surface-to-volume, which resulting in the brilliant photocatalytic degradation of AR under UV light.

Conclusion

Sol-gel synthetic route was used for in-situ synthesis of ZnO:Sm^{3+}(1 - 9 mol %) thin films. Crystallite size and Hexagonal Wurtzite structure of the ZnO:Sm^{3+} catalyst was confirmed by XRD results. ZnO:Sm^{3+} (1 - 9 mol %) catalysts prepared by the sol-gel route exhibits excellent photocatalytic activity under light, attributed due to morphology and higher content of oxygen vacancies. All the obtained results indicate that of Sm^{3+} activated ZnO material is a suitable prominent catalyst for the degradation of pollutants.

***Kiran T.* –** M.Phil in Chemistry, Assistant Professor of the Chemistry Department;
***Parveez Ahmed H.M.* –** PhD in Chemistry, Professor of the Chemistry Department;
***Noor Shahina Begum* -** PhD in Chemistry, Professor of the Chemistry Department;
***Karthik Kannan* –** PhD in Physics, Research Fellow;
***Radhika D.* -** PhD in Chemistry, Assistant Professor of the Chemistry Department.

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Т. Кіран[1], Г.М. Парвеез Ахмед[2], Нур Шахіна Бегум[3], Картік Каннан[4], Д. Радхіка[5]

Структурні, морфологічні та оптичні дослідження золь-гель тонких плівок ZnO, активованих Sm^{3+}, для фотокаталітичних застосувань

[1]Технологічний інститут, Бенгалуру, Карнатака, Індія, t.kiran0419@gmail.com
[2]Інженерний коледж Гусія, Раманагара, штат Карнатака, Індія, parru63@gmail.com
[3]Університет Бенгалуру, Карнатака, Індія, noorsb@rediffmail.com
[4]Центр перспективних матеріалів, Катарський університет, Доха, Катар, karthikkannanphotochem@gmail.com
5Інженерно-технологічний факультет, Джайн - Університет, Карнатака, Індія, radhikadv8@gmail.com

Тонкі плівки ZnO, активовані рідкісноземельними (RE) іонами, отримано золь-гель методом, і класифіковано різними методиками. Дослідження Х-променевої дифракції (XRD) вказують на гексагональну структуру типу вюрциту отриманих тонких плівок. Використано формулу Шеррера для розрахунку середнього розміру кристалітів (25 - 40 нм) з різними концентраціями Sm^{3+}. Оптичну ширину забороненої зони розраховано за спектрами дифузного відбиття (DRS). Барвник кислоти червоної (AR) розкладався під дією ультрафіолетового (УФ) випромінювання на наноструктуровані тонкі плівки ZnO: Sm^{3+} (1 - 9 мол.%). Найвища фотодеградація (95%) спостерігалася для 7 мол.% легованого Sm^{3+} ZnO. Усі отримані результати свідчать про те, що отриманий матеріал може бути добрим матеріалом у якості фотокаталізатора.

Ключові слова: ZnO: Sm^{3+}; тонкі плівки; XRD; DRS; фотокаталіз.