International Research Journal of Natural and Applied Sciences
Vol. 3, Issue 5, May 2016 IF- 3.827 ISSN: (2349-4077)
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INVESTIGATION OF ZINC DOPED BARIUM SULPHIDE NANOSTRUCTURES FOR PHOSPHER AND PHOTO-CATALYTIC APPLICATIONS

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ABSRACT

We have synthesized BaS:Zn nanocrystalline powder of average grain size 31 nm by solid-state diffusion method using sodium thiosulphate as a flux. The nanoparticles were characterized by UV-Vis, Photoluminous (PL), Photo-catalytic (PC), X-ray diffraction (XRD), Scanning electron microscopy (SEM), Electron diffraction spectroscopy (EDS), Transmisson electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR). The particle size of BaS nanoparticles as determined using Scherrer formula is found to be about 31 nm. The particle size is found to decrease in Zn doped BaS nanoparticles. UV-VIS spectroscopy was used to determine the band gap of these nanoparticles. The energy band gap of bismuth doped BaS nanopowder has been calculated to be 4.54 eV and is blue shifted in comparison to their bulk counterparts. On excitation by 425 nm, these nano phosphors give one emission peak at 575 nm which corresponds to green color. In the excitation spectra of these particles there are two peaks at 363 nm and 425 nm. The effect of dopant concentration on the photoluminescence of BaS:Zn nanocrystallites has been studied which is in agreement with the principle of concentration quenching.

Keywords – Nanocrystalline, photoluminescence, x- ray diffraction, quenching.

INTRODUCTION

Nanophosphors is one of the interesting subjects of nanotechnology. In the nanoscale range, structures and properties of material differ significantly from those of single atoms molecules and the bulk materials. Nanotechnology is a part of science and technology about the control of matter on the atomic and molecular scale – this means things that are about 100 nanometers or smaller. 'Nanotechnology ` refers to the projected ability to construct items from the bottom up, using techniques and tools being developed today to make complete, high performance products. Nanotechnology is defined as the study of structures between 1 nanometer in size. Nanotechnology will mean complete control of structure of matter, building complex objects with molecular precision. At nanoscale, molecular size starts affecting the properties of materials.

When the size of the nano crystal is smaller than the Bohr excitation radius of the material, they exhibit properties which are size dependent and distinct from the bulk . Such a material is a very promising one in electronics, data storage, energy storage, catalysis and sensors . It is, therefore, important to develop techniques which are simple, cost-effective, environment friendly, easily scalable and at the same time with parameters to control size and shape of the materials. Barium sulfide is an inorganic compound with the formula BaS. Barium (atomic symbol: Ba, atomic number: 56) is a block S, group 2, period 6 element with atomic weight of 137.27. Barium is a soft, silvery gray metal. Sulfur or sulphur (atomic symbol: S, atomic number: 16) is a block P, group 16, period 3 element with an atomic radius of 32.066. Barium sulfide is an important precursor to other barium compounds including $BaCO_3$ the pigment lithopone, ZnS/ $BaSO_4$. It is colorless, although like many sulfides, it is commonly obtained in impure colored forms. Barium sulfide is yellowish – green or gray lumps that are soluble in water. Barium sulfide is used in brown patinas as well as for dehairing hides, in flame retardants and luminous paints. It has rock salt structure. For the synthesis of CaS and SrS nanocrystallites containing different dopants, some methods like solvo-thermal, sol-gel, wet chemical co-precipitation, solid state diffusion have been successfully used. It was, therefore decide to synthesis BaS phosphors doped with bismuth by solid state diffusion method.

OBJECTIVES OF THE INVESTIGATION

Following the proposed objectives:

1) To Synthesize pure and Zn doped Barium Sulfide nanostructures

2) To investigate Crystallographic, topographic and morphological characteristics of the synthesized nanomaterials

3) To analyse Optical characters of the synthesized nanomaterials

4) To check photo catalytic activity of the synthesized nanomaterials

EXPERIMENTAL

For the synthesis of intrinsic and extrinsic BaS, solid state diffusion method was preferred. Chemicals used for synthesis of BaS nanoparticles were $BaSO_4$. Carbon powder of analytical reagent grade was used as the reducing agent. Sodium thiosulphate was used as flux. Zinc act as activator. The ingredients, barium sulphate (2 gm), sodium thiosulphate (0.2gm) and reducing agent carbon powder (5gm) were mixed for 2 hours with the help of good quality agate mortar and pestle. Stoichiometric ratio of Zinc(activator) and few drops of ethanol were added and the whole charge was mixed with help of mortar and pestle. Graphite crucibles were used for firing the charge. The prepared charge was placed in graphite crucible and a layer of carbon powder (reducing agent) was spread over it to maintain the reducing atmosphere. It was covered with another similar crucible. Both crucibles were placed in muffle furnance from room temperature to 900° C then fix the temperature at 900° C for 2-3 hours. After 2-3 hours, the charge was transferred to a mortar and was rapidly grind while red-hot. These powders were stored in culture tubes.

There are four **advantages** in this approach:

(a) simple, cheaper and convenient
(b) high yields
(c) At the same time, reduction and incorporation of activator can be achieved
(d) Involves less solvent and reduced contamination.

This method has already been used for synthesis of BaS, CaS and SrS based nanophosphors by Singh et al. The product were analysed by X-ray diffractograms using Rigaku Miniflex-600 powder X-ray diffractometer in 2θ range 20-70° keeping step size 0.02° at the scan speed of 4 deg./min. at generator tension of 40 kV and generator current 15mA. All measurements were carried out at room temperature. The morphology and sizes of the nanophosphors were determined by TEM carried out on a H-7500(Hitachi Ltd., Tokyo, Japan) operated at 120 kV. Diluted nanophosphors suspended in absolute ethanol were induced on carbon coated copper grid, and were allowed to dry in air. The absorption spectra of all the samples were recorded through double beam UV-vis. absorption spectrometer (Hitachi U-2900) in the wavelength range 200-800 nm**.**

RESULTS AND DISSCUSSION

X- RAY DIFFRACTION (XRD)

Fig. 1 shows the XRD pattern of BaS : Zn, the pattern confirms BaS with the rock salt type structure without any traces of impurity while there is a little shift in peak position due to Zinc. The average crystallite size was calculated by Debye-scherrer formula:

$$\mathbf{D=}\ \frac{\mathbf{0.89}\lambda}{\boldsymbol{\beta}\ \mathbf{cos}\ \boldsymbol{\theta}}$$

where:

D= Average crystallite size

λ = Incident X-ray wavelength (Cu α X-ray wavelength= 1.5409 A°)

β = Full width at half maximum (FWHM) of diffraction peak in radians

θ = Peak position in X-ray diffractogram.

It can be clearly seen from the recorded diffractograms that XRD peaks broaden with the addition of dopants in the host matrix. This peak broadening may be due to reduction of the crystallite size. Average crystallite size values calculated for intrinsic and extrinsic BaS nanocrystals are ~31nm.

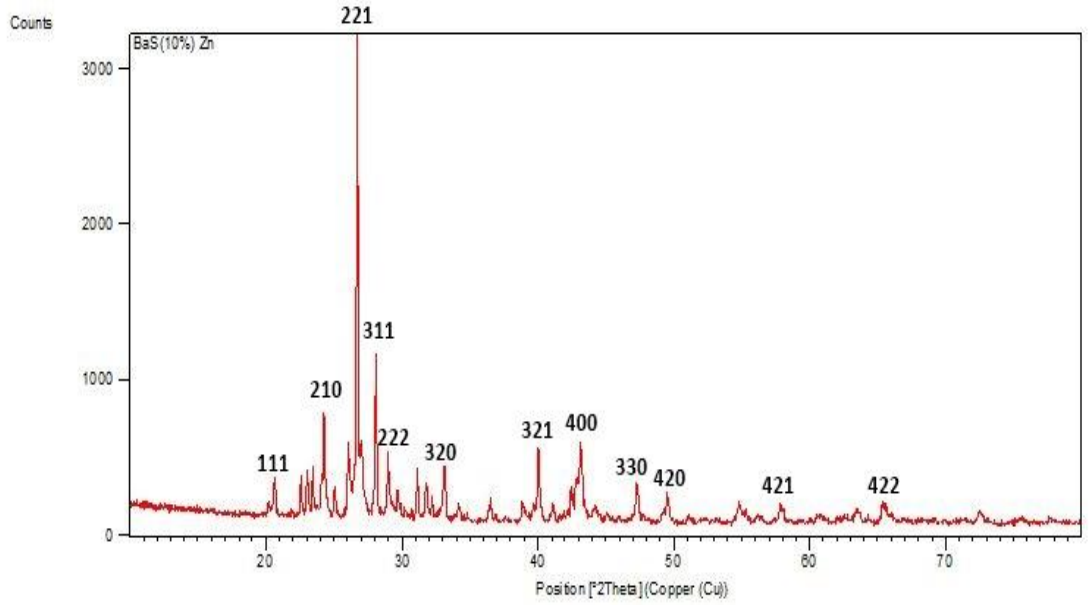
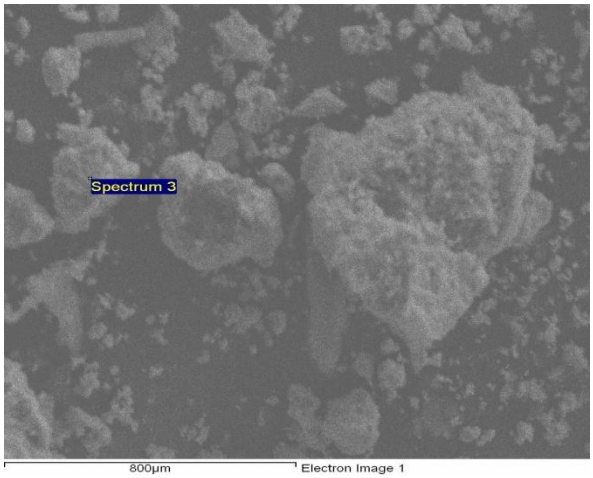


Fig. 1 XRD pattern for the BaS: Zn (10%) nanoparticles

SCANNING ELECTRON MICROSCOPE (SEM)

Fig. 2(a) shows the SEM micrographs recorded for synthesized BaS nanoparticles. The photography was not entirely clear because of the condensation and agglomeration of the nanopartices material as similar in the case of pure BaS nanoparticles.

Fig. 2(b) EDS analysis of $Ba_{0.9}Zn_{0.10}S$ nanoparticles which confirms the elemental compositions of $Ba_{0.9}Zn_{0.10}S$ nanoparticles. The confirmation of dopant is clear from EDS analysis.



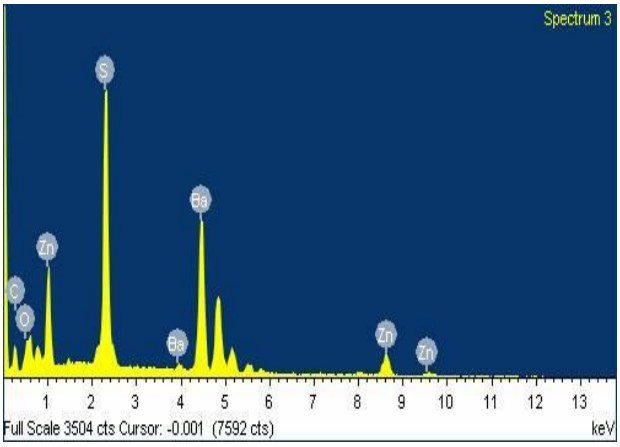
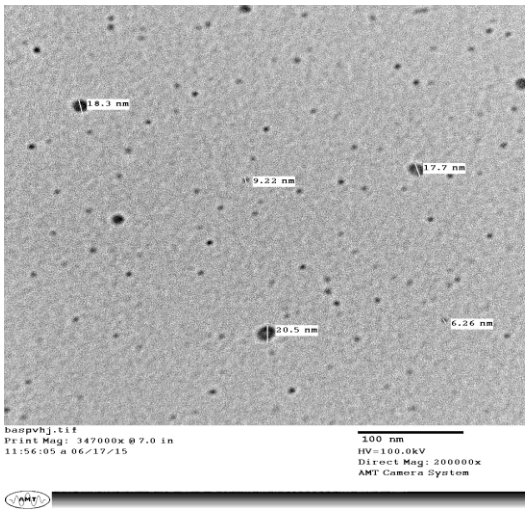


Fig. 2(a) **Fig. 2(b)**

SEM image of $Ba_{0.9}Zn_{0.10}S$ nanoparticles **EDS image of $Ba_{0.9}Zn_{0.10}S$ nanoparticles**

TRANSMISSION ELECTRON MICROSCOPY (TEM)

TEM micrographs of pure BaS and $Ba_{0.9}Zn_{0.10}S$ nanostructures recorded at 100 kV accelerating voltage and direct magnification of 150000X are shown in **Fig. 3(a) & 3(b)**. The morphology of BaS nanoparticles is found to be nearly spherical. Average particle size calculated from recorded micrographs is ~ 14 nm.



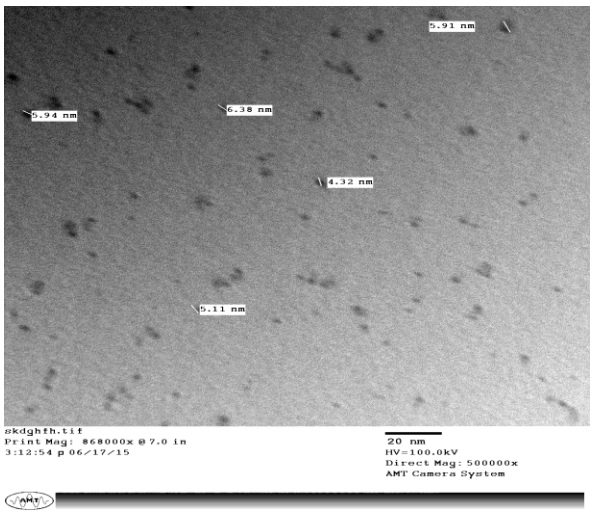


Fig. 3(a) **Fig. 3(b)**

TEM image of pure BaS nanoparticles **TEM image of BaS:Zn(10%)nanoparticles**

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Fig. 4 shows the FTIR spectrum of $Ba_{0.90}$ $Zn_{0.10}S$ nanoparticles synthesized by Solid State Diffusion method was acquired in the range of 4000-400 cm^{-1}. Few absorption peaks are observed between 400-800cm^{-1}. These peaks are attributed to Ba-S stretch. The band at 824 cm^{-1} is due to C–H out of plane bending. An absorption peak appearing around 1,047 cm^{-1} is due to C—N mode of the aliphatic amines. The band at 1,159cm-1 is due to C—H. The transmittance at 1,384 cm^{-1} is assigned to the deformation of N—H. An absorption peak appearing around 1,423 cm^{-1} is due to C—C stretch (in ring). The band at 1,635 cm^{-1} is due to ester C=0 stretching mode. The transmittance at 2,140 cm^{-1} is assigned to the alkynes CEC stretching. The absorption peak observed at 3432 cm^{-1} is attributed to 0–H stretching.

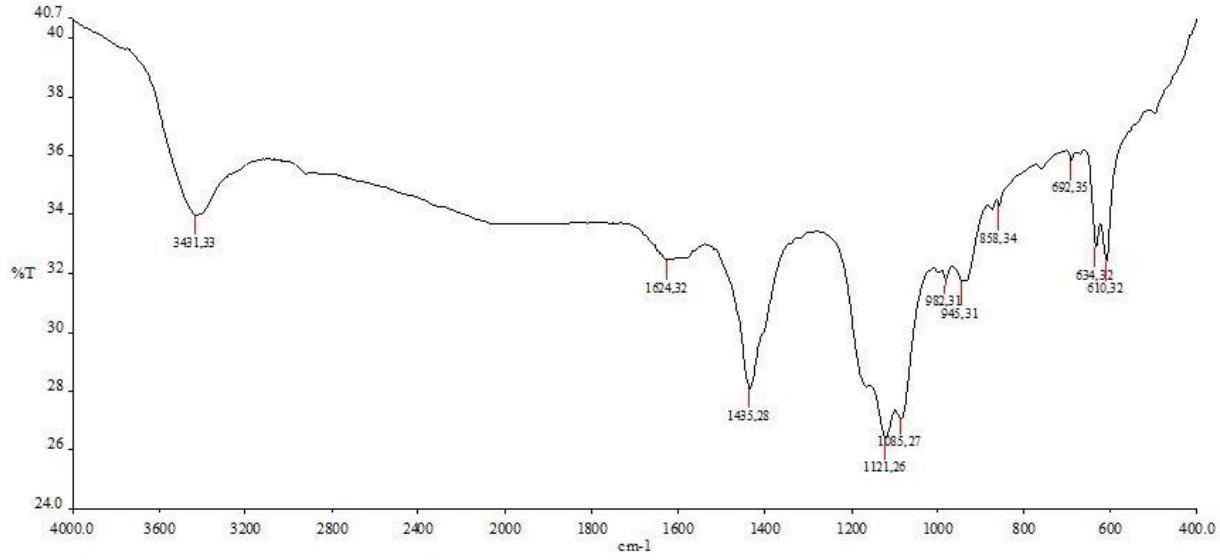


Fig. 4 shows the FTIR spectrum of BaS:Zn (10%) nanoparticles

UV-Vis. Absorption Spectroscopy

In **Fig. 5**, The spectra show broad absorption in UV range. The band gap of pure BaS and ZN(0.5%, 1%, 5%,10%) doped BaS samples are 4.584eV, 4.534eV, 4.550eV, 4.501eV and 4.584eV, respectively. The absorption edge wavelength increases and band gap decreases with increase in dopant concentration. Red shift in recorded spectra has been clearly observed with increasing dopant concentration.

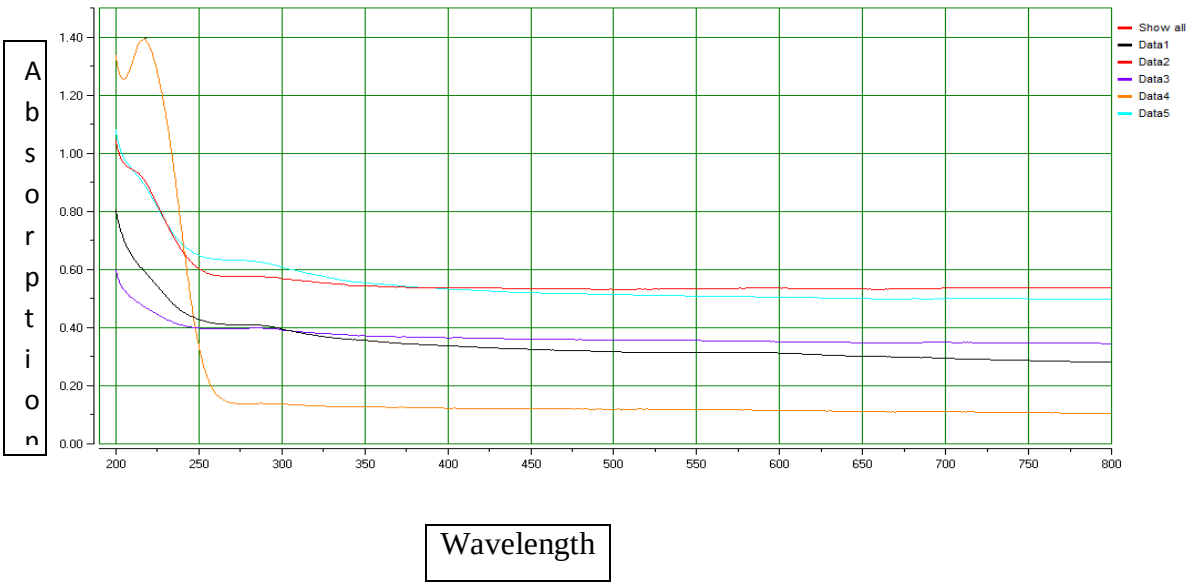


Fig. 5 UV-Vis. Absorption spectra of $Ba_{1-x}Zn_xS$ nanoparticles

PHOTOLUMINESCENCE

The room temperature PL spectra of the pure BaS and Zn-doped BaS nanoparticles recorded via excitation at 425nm have been shown in **Fig. 6**. The recorded emission spectra show the dichromatic emission spectra with broad emission peaks at ~363 nm and ~425 nm. The broad violet emission may be originating from the host related defect states. PL peak broadening indicates the broad particle size distribution, which also confirmed by TEM micrographs.

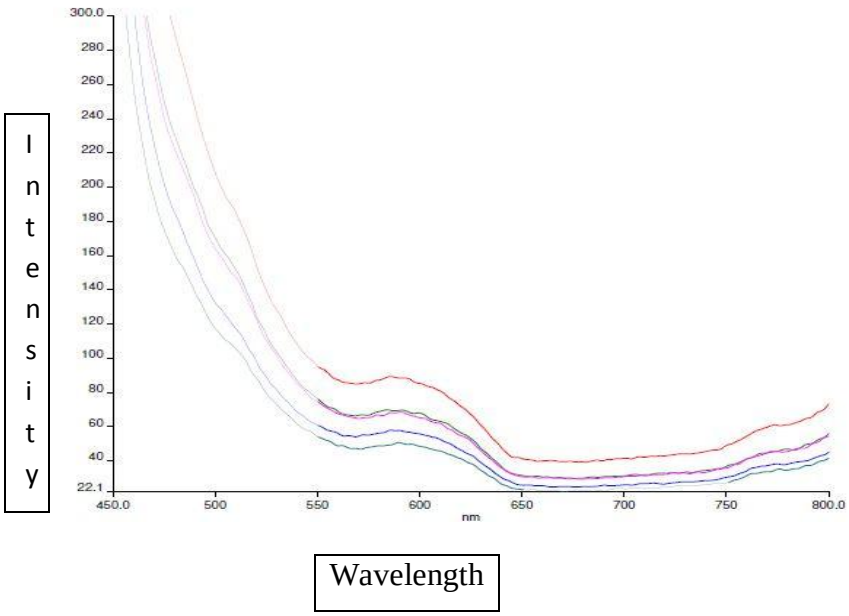


Fig. 6 PL Spectra of $Ba_{1-x}Zn_xS$ nanoparticles

PHOTOCATALYTIC ACTIVITY

In **fig. 7,** the spectra show the photocatalytic activity of BaS:Zn nanoparticles. The procedure of photocatalytic activity is given below:-

1.For stock solution, 3g of methylene dye was taken and dissolved in 500 ml of distilled water. After this stock solution was placed in dark.

2. Take 100ml of stock solution in a bowl.

3. Now pour the 0.05 gm of synthesized BaS nanoparticles in the bowl.

4. Place the bowl on magnetic stirrer for one hour stirring in dark.

5. After one hour 5ml solution was taken from the bowl with the help of a pipette and pours the solution in test tube.

6. Switch on the UV tubes, 15 minute exposure to the solution was given and also switch on the magnetic stirrer.

7. After 15 minute switch off the UV tubes and magnetic stirrer, take 4-5 ml solution from the bowl with the help of a pipette and pour the solution in test tube. Repeat the step 7 for 8 times.

9. Repeat the whole experiment for different doping concentrations of Zn.

10. Then record the absorption spectra of these solutions using UV-visible absorption spectrometer.

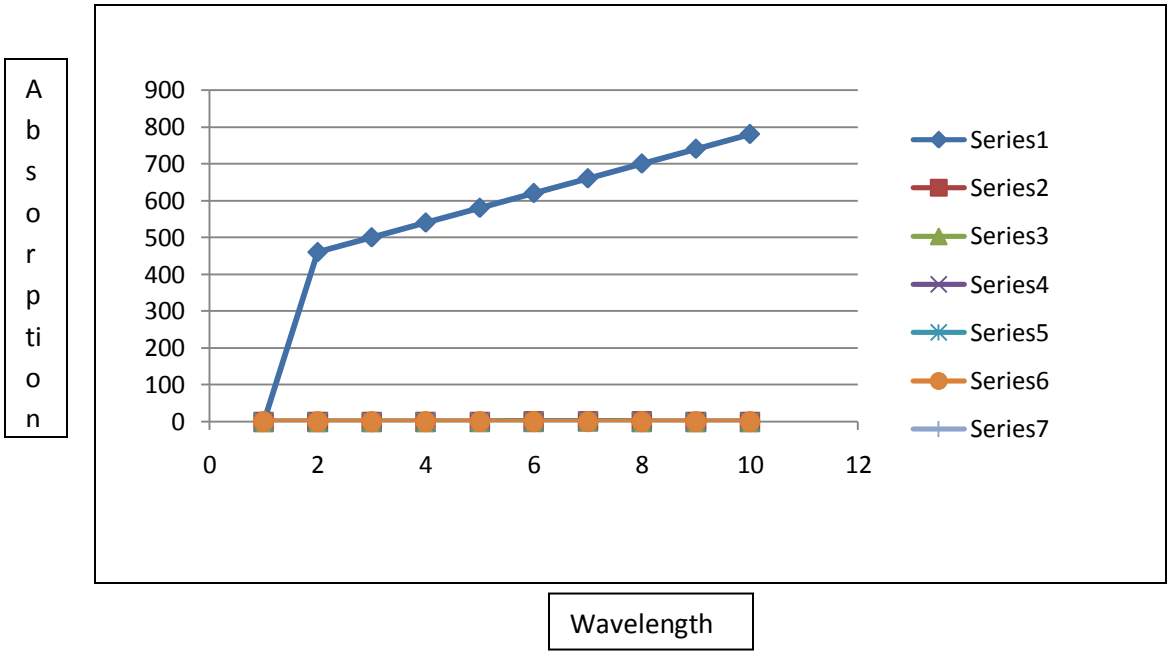


Fig. 7 Photo- catalytic spectra of $Ba_{1-x}Zn_xS$ nanoparticles

CONCLUSIONS

Solid-state diffusion method was used for preparation of BaS: Zn nanophosphors. The energy band gap of bismuth doped BaS nanopowder has been calculated to be 4.54 eV and is blue shifted in comparison to their bulk counterparts. The particle size of BaS nanoparticles as determined using Scherrer formula is found to be about 31 nm. The particle size is found to decrease in Zn doped BaS nanoparticles.

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