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# SYNTHESIS, CHARACTERIZATION AND THERMOLUMINESCENCE BEHAVIOR OF (Cd, Zn)S MIXED PHOSPHOR DOPED WITH SILVER

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(Cd,Zn)S:Ag with particles size of about 175nm has been prepared by the solid state method. The effects of solid state synthesis method on luminescence characteristics are investigated.The Optical band gap was found 3.35 eV by the Transmission Spectra of the (Cd,Zn)S:Ag. The thermoluminescence glow curve of (Cd,Zn)S:Agwas recorded for 5, 10, 15, 20 and 25 min UV exposure time. The Peak temperature was found to be 107°C for all exposure time, show linear response with UV dose. The kinetic parameter such as activation energy, frequency factor and order of kineticswere calculated by using Peak shape method and also calculated the trap depth by using different formulas. The value of the activation energy belongs to 0.49eV to 0.59 eV and frequency factor $3.7X10^{7}$ $s^{-1}$to$1.23X10^{9}s^{-1}$.

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## 1. Introduction

In past years, II–VI compound semiconductor phosphor have been paid great attention owing to their unique optical properties that by changing the particle size as well as by changing the compositions.Amongthese, CdS and ZnS phosphors have attracted considerable attention fromthe research community because of their wide band gap and tremendous potential applications in diverse areas such as solar cell, photo-catalysis, sensors, photonic, photonic devices, X- ray absorber, cathode-ray tube devices, optoelectronic devices and due to theirunique physical properties having another potential applications such as photo-electronics, optoelectronics, acousto-optic properties and quantum radiophysics, are closely connected with its unique crystallographic properties because of its capability of undergoing polymorphictransformations, and this makes additional structural investigations of interest [1-5]. Phosphors based on (Cd,Zn)S host materials doped with Ag is an efficient X-ray to light converter and a sufficient X-ray absorber [6]. In most instances, it has been possible to optimize and improve the performance of the devices significantly by improving the characteristics of the phosphors themselves [8-9].

(Cd,Zn)Sphosphor have been prepared by various techniques, such as solid state reaction [10] , successive ionic layer adsorption and reaction (SILAR) [11] chemical bath deposition [12,13], spray pyrolysis[14] and metalorganic chemical vapour deposition [15] and wet chemical precipitation method [16]. Among these, solid state reaction method is economical, simpler and more versatile than the others and gives the possibility of obtainingphosphor with

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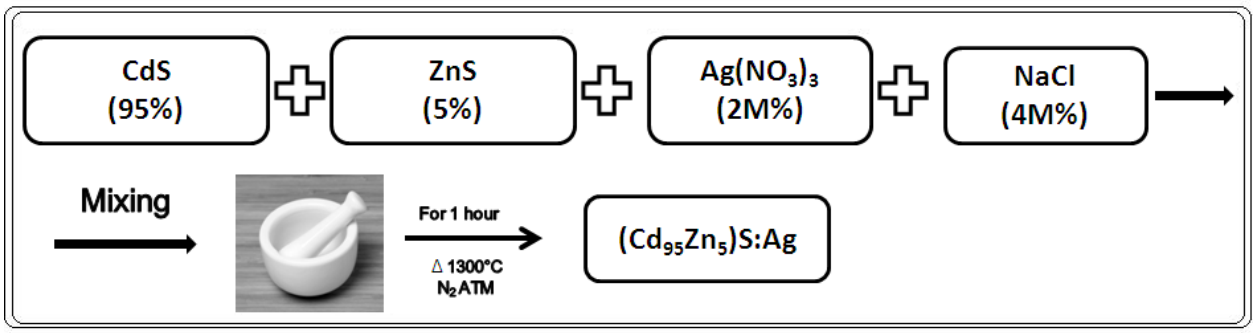
suitable properties for optoelectronic applications and also when large areas are needed. The method is well studied and produces qualalitativephosphor that have comparable structural and optoelectronic properties to those produced using other sophisticated t techniques [14, 16]. Here, for preparing (Cd, Zn) S: Ag phosphor solid state synthesis has been adopted. Solid state synthesis is a versatile, simple and slow process, which allows effective synthesis of a variety of solid crystalline phosphors. For the (Cd,Zn)S phosphor family, with increasing ZnS content, the color of light emitted by this phosphor family changes from green to orange through blue, yellow, and red respectively.All CdS-ZnS phosphors have the advantages of high efficiencies in addition to low persistence.

In recent years, novel applications in medical dosimetry requirethe development of new phosphors, which can be employed as thermoluminescence(TL), radioluminescence (RL) or optically stimulatedluminescence detectors. They should have high sensitivity, chemicalstability and optical and mechanical properties. Althoughthe discovery of new compounds is of the utmost importance, thedevelopment of these materials is also focused on the betterknowledge and control of microstructure and optical properties ofexisting dosimetric materials.(Cd,Zn)S phosphor doped with Ag ion has been paid a great attention by several researches because of its commercial application as a blue emitting phosphor [11,16].

## 2. Synthesis

The silver-doped (Cd,Zn)S mixed phosphor was prepared by using the solid state reaction method.A mixture of analyticalgrade CdS and ZnS (Fluka, Switzerland), Silver nitrate $AgNO_3$ and sodium chloride according to stoichiometric ratio. The $Ag^+$ ion concentration was fixed at 2 mole percent and CdS and ZnS content were fixed at 0.95 and 0.5 percent, respectively. The Mixture was transferred in aquartz tube and placed in a silica tubular furnace. The furnace temperature was maintained at 1100°C and the mixture in quartz tube was heatedfor 1 hour in an inert atmosphere of flowing nitrogen gas. After the heating was complete, the mixture was taken out of the furnace and immediately crushed and finely powdered to have a uniform particle size. Although defects are produced during grinding, but better repetitive results are obtained in the case of ground phosphors as compared to those in ungrinded phosphors.(Scheme 1).




*Scheme 1.Synthesis of (Cd,Zn)S:Ag.*

The absorption coefficient (α) and the band gap is determined using the transmission measurement carried out in an UV-VIS Spectrophotometer in the wavelength range 300nm – 900nm.. To determine the average particle size and the phase of the samples, X-ray powder diffraction (XRD) pattern was measured by using a D-8 Advance diffractometer (IUC INDORE) with Cu K*a* radiation. The morphology of the phosphor was characterized by scanning electron microscope (SEM) [Model: JEOL-JSM 5600] and transmission electron microscopy (TEM) [JEOL JEM- 3010].The Thermoluminescence (TL) glow curve wasrecorded with the help of TLD reader (Model 1009I) made by Nucleonix fitted with 931B photomultiplier tube (PMT) by taking 1 mg of sample each time.For recording TL, samples were exposed to UV radiation from UVGL-58 handled UV lamp operating at 230V-50 Hz (emitting 254nm) for 5 to 25minutes

## 3. Results and discussion

### 3.1 Transmission Spectra

The optical transmission of the (Cd,Zn)S:Ag phosphor was recorded using double beam UV-Visible spectrophotometer in the wavelength range 300 nm – 950 nm and the transmission spectra is presented in fig. 1[a]. The optical data is used to evaluate the absorption coefficient (α), energy band gap (Eg) and nature of transition involved. Optical energy band gap (Eg) can be calculated using absorption coefficient (α). The experimental values of $(\alpha)^2$ plotted against photon energy ($E_{ev}$) for (Cd,Zn)S:Ag phosphor was shown in Fig. 1[b]. The optical band gap was found 3.35 eV[5,10,14].

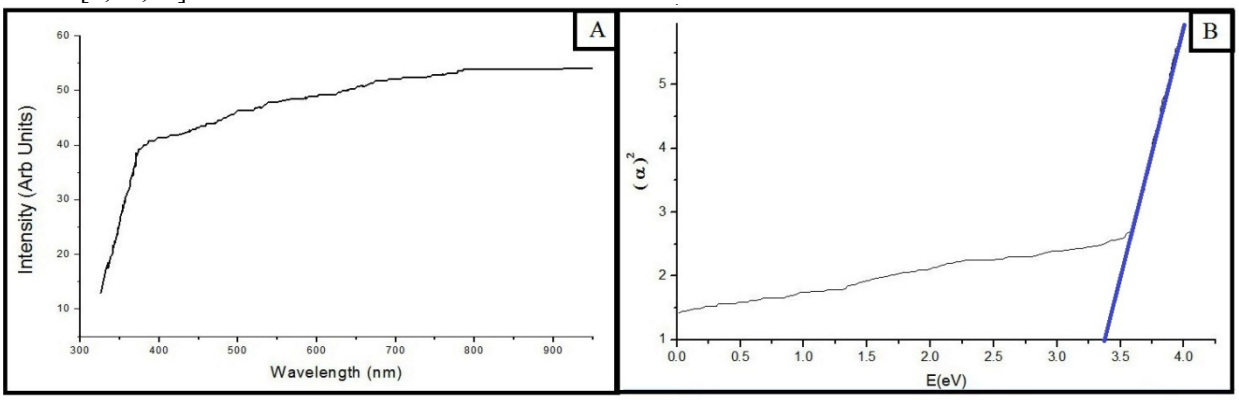



*Fig. 1[a].Transmission spectra of (Cd,Zn)S:Ag;[b].Square of the absorption co-efficient with Photon energy of (Cd,Zn)S:Ag*

### 3.2 X- Ray Diffraction Analysis

Figure 2shows the XRD pattern of synthesized (Cd,Zn)S:Ag phosphor. The characteristic XRD pattern of the (Cd,Zn)S:Agphosphor exhibit many prominent peaks, they are about $24.05^0$, $26.35^0$ ,$28.17^0$, $48.46^0$ $54.75^0$ $59.87^0$ and $61^0$.These peaks are originated from (1 0 0), (0 0 2), (1 0 1), (1 0 3), (0 0 4), (2 0 2) and (104) planes respectively. These diffraction pattern are in good agreement with JCPDS card number 49-1302 [12]confirmed Hexagonal structure. The average particle size (D) of the as-formed (Cd,Zn)S:Agphosphor was estimated from the full width at half maximum (FWHM) of the diffraction peak of the powders, using Scherrer's formula [18].

$$D = .09\lambda/\beta\cos\theta$$

Where λ is the wavelength of X-ray used, θ the Bragg angle and ß is the Full width at half maxima (FWHM) of corresponding peaks. The average crystallite size was found 175nm.

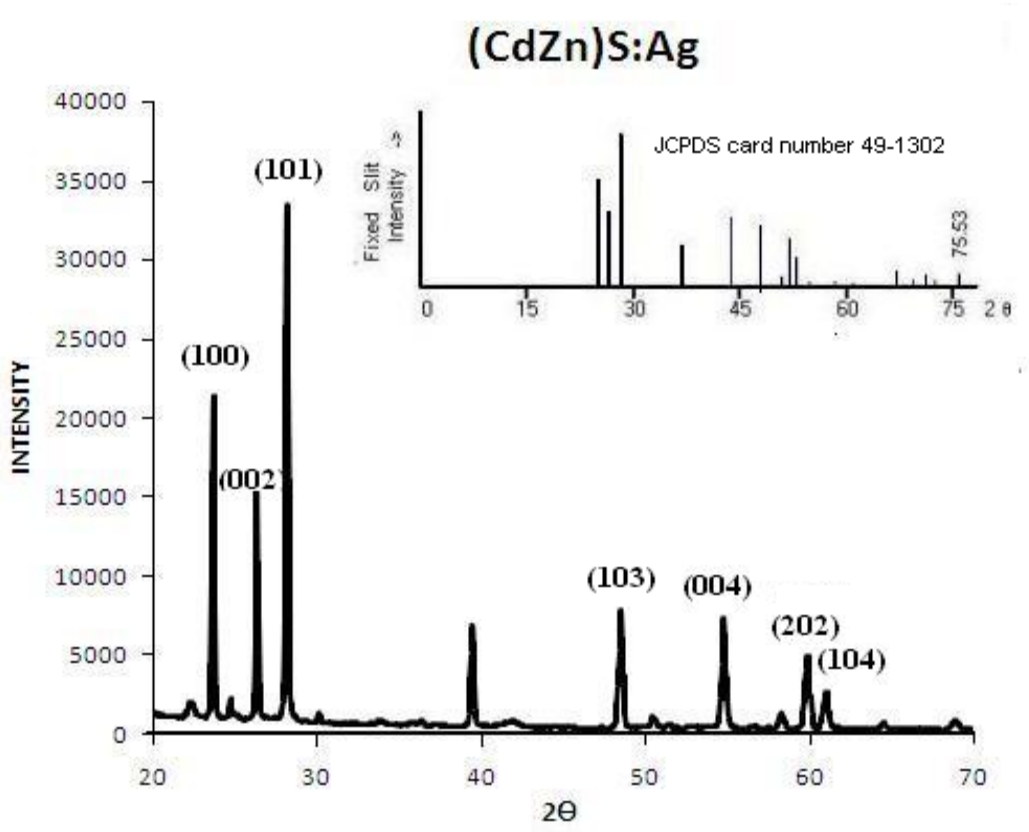



*Fig. 2. XRD pattern of (Cd,Zn)S:Ag*

### 3.3 Scanning Electron Microscope (SEM) Results

Figure 3shows the SEM micrograph of (Cd,Zn)S:Agsynthesised by the Solid state method. By the SEM image of (Cd, Zn) S: Ag phosphor, morphology and size were determined. The diameter of the phosphor was in the range of 150 to 200 nm, and the spherical particles were agglomerated.

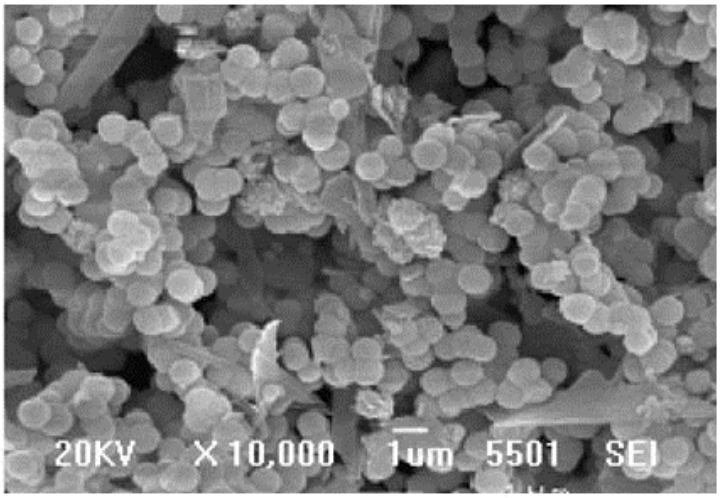



*Fig. 3. SEM image of (Cd,Zn)S:Ag*

The statistic histogram is shownin Figure 4., where the Gaussian's fitting was also carried out. Thedifference between the average size confirmed from SEM and the crystallographic size derived from XRD is probably due to thereasons that, on the one hand the crystallographic size

calculationbased on the Debye–Scherrer equation in the case of larger sizeparticles may introduce larger error, on the other hand the crystallographicsize reflects the size of well-crystallized part of theparticles, but the average size observed from SEM presents theapparent size of the particles, thus they may be different.

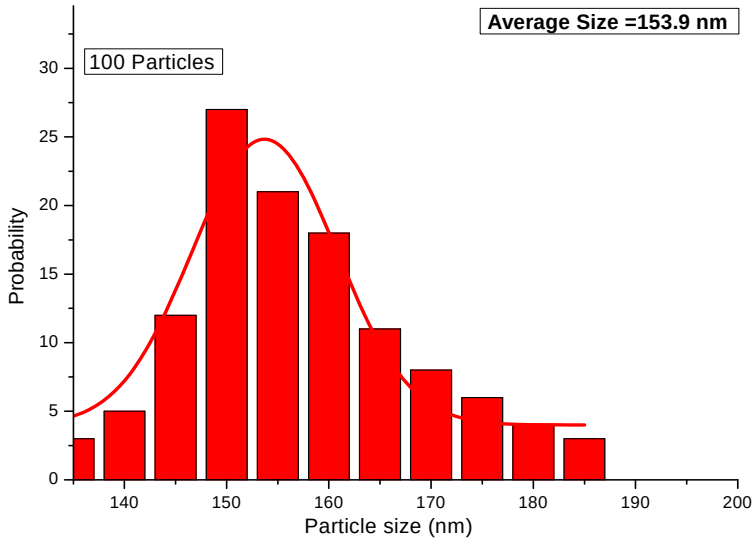



*Fig. 4.Histographof particle size distribution for the studied (Cd,ZnS):Agphosphors*

### 3.4 TEM Result

To assess the size and microstructure of the particletransmission electron microscopy (TEM) study has been performed. Figure 5**s**hows an abundance of nearly spherical crystallites, which have a particle size of 151nm.

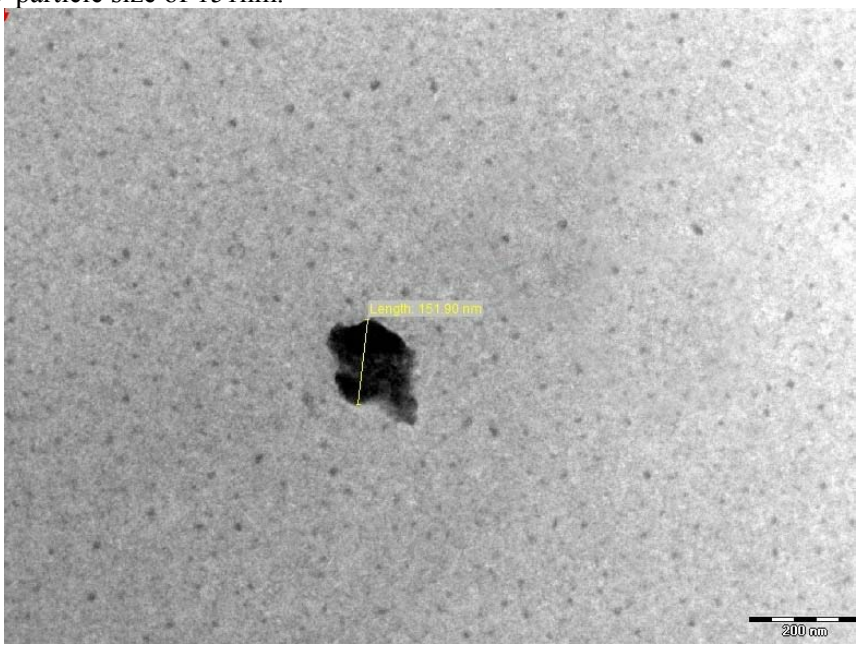



*Fig. 5. TEM result of the (Cd,Zn)S:Ag*

### 3.5 Thermoluminescence glow curve of (Cd,Zn)S:Ag phosphor

Thermoluminescence (TL) is a well known phenomenon which is caused by the thermally assisted release of the irradiation induced electrons from the traps of the material. The TL curve

can provide valuable information about the intrinsic defect of materials and the energetic ray to which the material was subjected. Therefore, it is widely applied in the field of defect studying, dating in archeology, irradiation detection, etc.The TL glow curve for (Cd, Zn) S: Ag phosphor was recorded with a UV exposure of 5 minup to25 min at a heating rate $5^0Cs^{-1}$. The order of kinetics, activation energy and frequency factor has calculated using Chen's empirical formula [19].Figure5shows the TL glow curve of (Cd,Zn)S:Ag with the variation of UV exposure time.The kinetic parameter of (Cd,Zn)S:Ag phosphor are listed in Table 1.In this TL glow curve shape factor $\mu \approx 0.52$ or greater than second order kinetics may be caused by the presence of two or more traps with similar trap energies. Here the value of μis found between 0.56 & 0.57 for 5 minute upto25 minute, which shows the second order kinetics.The value of the activation energy belongs in the range of 0.49eVtoo.59 eV and frequency factor $3.7X10^7$ to$1.23X10^9$.The trap depth of (Cd,Zn)S:Ag phosphor has also been calculated by using the different methods and listed in table 2 [10,20-27]. Figure 6 show the linear response of the (Cd,Zn)S:Ag phosphor with UV exposure time. As the exposure time increases the intensity should increase linearly with it.

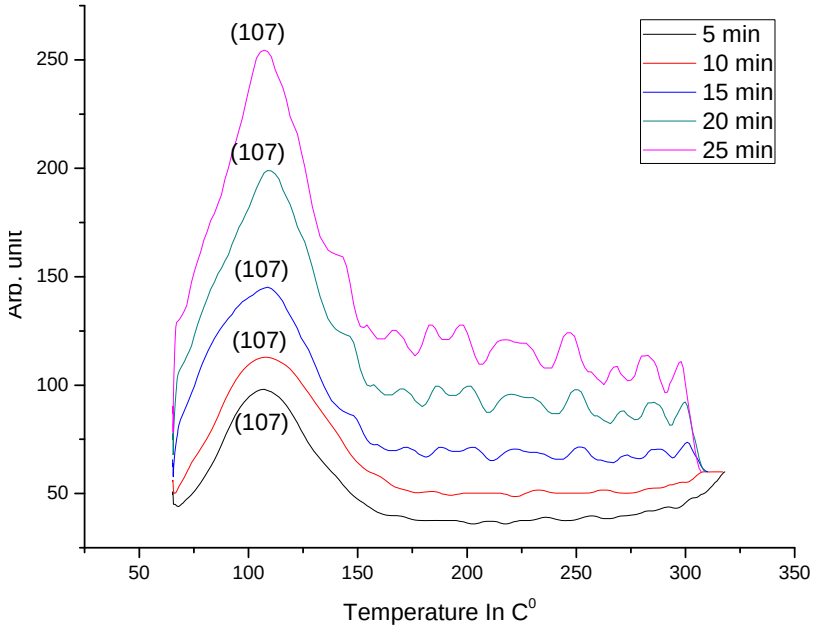



*Fig. 6.TL Glow curve of (Cd,Zn)S:Ag phosphor*

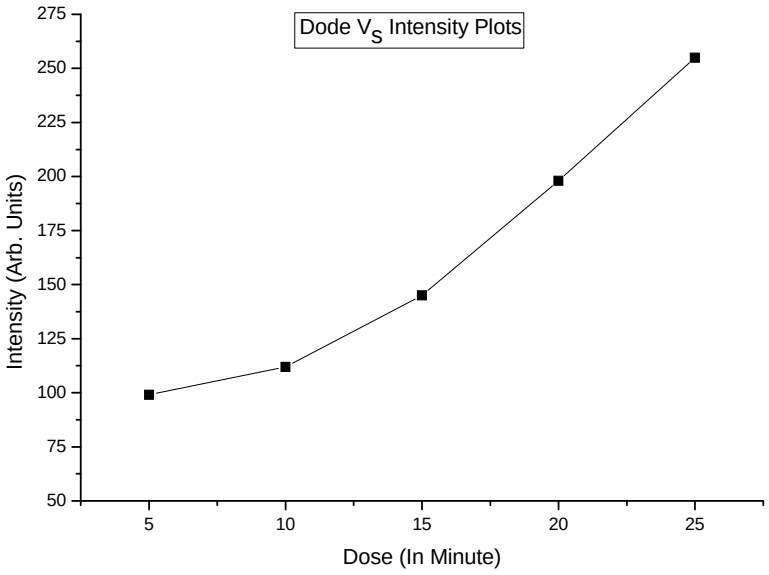



*Fig. 7. Dose $V_s$Intenstiy plot of (Cd,Zn)S:Ag phosphor*

*Table 1. Kinetic Parameters (Cd,Zn)S:AgTL glow curve*

| UV Exposure time | $T_1$ (K) | $T_m$ (K) | $T_2$ (K) | τ | δ | ω | μ = δ / ω | Activation energy E in eV | Frequency factor S In $s^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| 5 | 348.77 | 380 | 422.75 | 31.23 | 42.75 | 73.98 | 0.57 | 0.61 | $1.92 X10^9$ |
| 10 | 345.47 | 380 | 439.51 | 34.53 | 59.51 | 94.04 | 0.63 | 0.57 | $4.9X10^8$ |
| 15 | 342 | 380 | 422 | 38 | 42 | 80 | 0.52 | 0.49 | $3.9X10^7$ |
| 20 | 352 | 380 | 425 | 28 | 45 | 73 | 0.61 | 0.69 | $2.58X10^{10}$ |
| 25 | 353 | 380 | 431 | 27 | 51 | 78 | 0.51 | 0.51 | $9.12X10^7$ |

*Table 2. The trap depth for the prominent glow peaks of the studied (Cd,Zn)S:Ag, evaluated from Second order kinetics*

| Methods | Activation energy, E (eV) UV exposure time in Minute | | | | |
|---|---|---|---|---|---|
| | 5 | 10 | 15 | 20 | 25 |
| E (eV) = $T_m$(K)/500 | 0..76 | 0..76 | .76 | .76 | .76 |
| $E(eV) = 23KT_m$ | 0.75 | 0.75 | .75 | .75 | .75 |
| $E(eV) = 38KT_m$ | 1.24 | 1.24 | 1.2 | 1.2 | 1.2 |
| $E(eV) = \frac{2KT_m^2}{\delta}$ | 0.58 | 0.41 | .59 | .55 | 48 |
| $E_\omega = C_\omega \frac{KT_m^2}{\omega} - b_\omega(2KT_m)$ | 0.59 | 0.52 | .46 | .67 | .68 |
| $E_\tau = C_\tau \frac{KT_m^2}{\tau} - b_\tau(2KT_m)$ | 0.61 | 0.57 | 43 | .74 | .81 |
| $E_\delta = C_\delta \frac{KT_m^2}{\delta} - b_\delta(2KT_m)$ | 0.58 | 0.49 | .48 | .63 | .62 |

## 4. Conclusion

(Cd,Zn)S:Ag phosphor with hexagonal structure was successfully synthesized by using easiest and low cost solid state reaction method. Particle size is calculated by using Powder X- ray diffraction technique. The particle size is found to be 175 nm. The scanning electron microscope (SEM) result was agreed with XRD result. We have investigated the thermoluminescence glow curve of (Cd,Zn)S:Ag phosphor. The TL intensity increases with increase in UV exposure time and it is maximum for irradiation time 25 min. It shows the linear response. The value of the activation energy belongs to 0.49 eVtoo.59 eV and frequency factor $3.7X10^7 s^{-1}$to$1.23X10^9 s^{-1}$. Prepared phosphor may be useful for thermoluminescence dosimetric studies.

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