Effect of Zn doping on the structural, compositional, thermoelectric and thermal conductivity properties of CdZnS thin films deposited by chemical bath deposition method.

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Abstract— The current study is focusing a lot on Zinc doping at different levels (5, 10, 15, and 20 wt%) in Cadmium sulfide thin films. These films are made using the chemical bath deposition method and are grown on glass substrates. The X-ray diffraction patterns show that the Zn-doped CdS films have a hexagonal wurtzite crystal structure. The study also looks at microstructural features like crystal size, lattice constants, microstrain, and dislocation density in the films. The surface structure of the films is examined using scanning electron microscopy. The presence of Zinc in the CdS films and their elemental composition is confirmed through energy dispersive X-ray analysis (EDAX). The negative Seebeck coefficient measured in thermoelectric power tests shows that the material behaves as an n-type semiconductor. At room temperature, the carrier concentration in the Zn-doped CdS films ranges from $4.1x10^{19}$ to $10.5x10^{20}$ cm^{-3}, indicating that the films are degenerate semiconductors. The rise in thermal conductivity of the Zn-doped CdS films is because of the increased carrier concentration. The electronic thermal conductivity of these films slightly decreases with rising temperature due to electron-phonon scattering and defects in the thin films at higher temperatures.

***IndexTerms*— Zn dopind CdS, thin films, Structural properties, compositional properties, thermoelectric properties.**

I. INTRODUCTION

CdS, ZnS, and CdZnS have been used in many optoelectronic devices. The process of making thin films from ternary semiconductor materials has been studied a lot in recent years because these films are important for making solar cells due to their good electrical and optical properties [1]. Ternary semiconductors are very important in heterojunction solar cells and photoconductive devices because cadmium zinc sulfide (CdZnS) thin films have a wide bandgap. The II-VI compounds are known for their photoconductivity and are used in various applications, including photovoltaic solar energy and thin film transistor electronics [2]. Ternary chalcogenide semiconductors like CdZnX (where X is S or Se) are gaining interest because they allow for changes in optoelectronic properties. These semiconductors have a wide direct bandgap ranging from 2.4 to 3.7 eV. By changing the ratio of Cd to Zn, these materials are used in a variety of technologies, such as blue and ultraviolet laser diodes, window layers for solar cells, antireflective coatings for infrared devices, electroluminescence, and low-voltage cathode luminescence [3]. Research on adding zinc to CdS improves its optoelectronic properties and is useful for photovoltaic, electronic, and optoelectronic devices. Zinc is an important element with a smaller ionic radius (0.074 nm) than cadmium (0.097 nm), allowing it to fit into the CdS crystal lattice or take the place of cadmium ions [4]. Adding zinc to CdS increases its resistivity and reduces diffusion length [5]. The large bandgap makes the film transparent across all parts of the solar spectrum and reduces absorption losses [6]. Ternary semiconductors are very important for studying thermoelectric properties because they perform well in this area. The thermoelectric power depends on the figure of merit, which is calculated using the formula:

$$ZT = (S^2\sigma T)/k \quad (1)$$

where S is the Seebeck coefficient, σ is the electrical conductivity (1/ρ), T is the absolute temperature, and k is the total thermal conductivity, which includes electronic (k_e) and lattice (k_L) contributions [7]. Thermoelectric measurements of semiconductors can provide information about the effective mass of charge carriers, free carrier concentration, and the scattering mechanisms. Several techniques, such as spin coating [8], sputtering [9], chemical vapour deposition [10], chemical bath deposition [11], vacuum evaporation [12], spray pyrolysis [13], sol–gel [14], and successive ionic layer and reaction (SILAR) [15], are used to prepare CdZnS thin films. Compared to other methods, chemical bath deposition offers advantages like low cost, simple equipment, low energy use, easy material composition changes, and quick production of uniform thin films at low temperatures and over large areas [16]. The main goal of this study is to make CdS thin films with zinc diffusion using a low-cost chemical bath deposition method. These films can be used as window layers in thin film solar cells. Although many researchers [17–22] have studied the structural, electrical, and optical properties of Zn-doped CdS samples, detailed studies on their thermoelectric properties are still limited, and there are few reports on the thermoelectric properties of Zn-diffused CdS thin films in the existing literature.

2. Experimental Procedures:

2.1. Materials:

All chemicals used for preparing Zn doped CdS films were of A.R. grade as follows: cadmium chloride [$CdCl_2$] (Loba Chem.), Zinc chloride [$ZnCl_2$] (Loba Chem.), triethanolamine [$C_6H_{15}NO_3$] (Loba chem.), ammonium hydroxide [NH_4OH] (Loba Chem.), and thiourea [NH_2-CS-NH_2] (Loba chem.). For the deposition of Zn doped CdS thin films, solutions of $CdCl_2$, $ZnCl_2$, and $(NH_2)_2CS$ were prepared separately using ammonia solution.

2.2. Preparation of Zn incorporated CdS thin films:

The method for growing the material starts with the reaction between Cd^{2+}, Zn^{2+}, and S^{2-} ions in a liquid solution. The first source of sulfur, which is NH_2-CS-NH_2, is dissolved in an ammonia solution (with a pH of at least 9) at room temperature, creating a solution of thiourea that is not very stable. In this solution, the thiourea breaks down to release S^{2-} ions. Next, a specific

amount of $CdCl_2$ and $ZnCl_2$ solutions are added to the ammonia solution to get the right amount of zinc—5%, 10%, 15%, or 20% by weight. All three solutions are mixed together in a single beaker that has already been cleaned glass substrates placed inside. The ammonia solution with S^{2-} ions helps reduce the $Zn(NH_3)_2^{2+}$ and $Cd(NH_3)_2^{2+}$ complexes into free Zn^{2+} and Cd^{2+} ions in the solution. This entire process happens in the presence of triethanolamine (TEA), which acts as a complexing agent, and results in the formation of uniform CdZnS thin films on the vertically positioned glass substrates. This takes place at a bath temperature of 800°C for one hour. Before the process starts, the glass substrates are cleaned with double-distilled water, acetone, and then placed in an ultrasonic cleaner. After the films are formed, the substrates are taken out of the reaction bath and rinsed with double-distilled water. The films are then dried on a hot plate at 100°C for 10 minutes and then heated in a furnace at 200°C for one hour. Finally, the films are stored in an airtight container. The resulting films are evenly spread, have high reflectivity, stick well to the substrate, and have a yellowish color, as shown in the photograph in Figure 1.

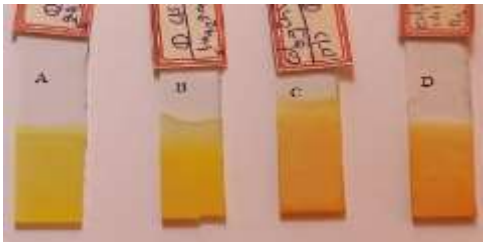

Fig. 1. As deposited Zn doped CdS thin fims(A-5,B-10,C-15,D-20 wt%)

2.2 Characterization*:*

The crystal structure and how the films are arranged in terms of crystal direction were studied using an X-ray diffractometer. The model used was the Bruker AXS D8 Advanced X-ray diffractometer from Germany, which uses Cu-Kα radiation with a wavelength of 0.15423 nm. The diffractometer was operated at 40 kilovolts and 100 milliamps, with an angle of 1 degree. The scan range covered 2θ from 20 degrees to 80 degrees. The surface shape of the films was examined using a scanning electron microscope (SEM). The model used was JOEL-JSM 5600 from Oxford Instrument analytical limited, 2000. The composition of the material in the thin films was determined using energy dispersive X-ray analysis (EDAX) with the same JOEL-JSM 5600 model. The thickness of the CdZnS material was measured using the weight difference method. The film thickness ranged from 205 to 295 nm, corresponding to deposition times between 50 to 80 minutes. The thermoelectric power (TEP) was measured using the integral method as described in reference [23]. The setup for this measurement was provided by "Pushpa Scientific Co., Hyderabad." The setup allows one end of the film to be connected to a heater and the other end to a large copper block to keep the temperature stable. It was observed that the cold end temperature was maintained at room temperature, 303K, while the temperature of the other end could be raised from 303K to 473K. The temperatures at both ends were measured using a copper constantan thermocouple attached directly to the film. The voltage (thermoelectromotive force) generated across the film was measured in relation to copper, as a function of the hot end temperature, using a high impedance digital micro voltmeter model DMV-001 supplied by "Scientific Equipment Roorkee."

3. RESULTS AND DISCUSSION:

3.1 X‑ray diffraction studies:

Figure 2: X-ray diffraction (XRD) patterns of 5 wt%, 10, 15 wt% and 20 wt% of Zn in CdS thin films Fig. 2 shows X-ray diffraction (XRD) patterns of CdS thin films with different amounts of Zn, measured in weight percent. All the patterns showed some broadening, which suggests the films are not very thick. The films had strong diffraction peaks at (1 0 0), (0 0 2), (1 0 1), and (1 1 0), and they were mostly oriented along the (1 0 1) direction, as shown in Table 1. These peaks matched well with standard patterns from JCPDF numbers 49-1302 and 40-0835, and they agreed with previous studies on CdZnS [24,25]. The XRD results confirmed the phase and purity of the thin films, and no extra peaks from oxides or other sulphides were found. As the Zn content increased, the diffraction peaks shifted to higher angles, showing a change from hexagonal CdS to cubic ZnS. This happened because Zn^{2+} ions, which are smaller than Cd^{2+} ions (0.97 Å) and S^{2-} ions (1.84 Å), replaced some of the Cd^{2+} ions in the crystal structure. This caused the lattice to distort. As more Zn was added, the lattice constant of CdS decreased slightly, from 0.4706 nm to 0.4619 nm. This shrinkage in the lattice is due to the difference in ionic sizes, which caused strain in the material. The full width at half maximum (FWHM) of the (1 0 1) peak increased from 0.56° to 1.12° as Zn concentration went up. The size of the crystallites, calculated using the Scherer formula, decreased from 15.23 nm to 7.62 nm as Zn content increased from 5wt% to 20wt%. The number of crystallites per unit area, calculated using the formula $N = t/D^3$, where t is the film thickness and D is crystal size, went up from 0.58×10^{17} m^{-2} to 6.66×10^{17} m^{-2}. This increase was because the crystals got smaller. Similar findings have been reported by Shubhas Chander et al. [27]. The microstrain (ε) and dislocation density (δ) of the films were calculated using equations from earlier studies [28, 29]. The microstructural details of the Zn-doped CdS thin films are listed in Table 1.

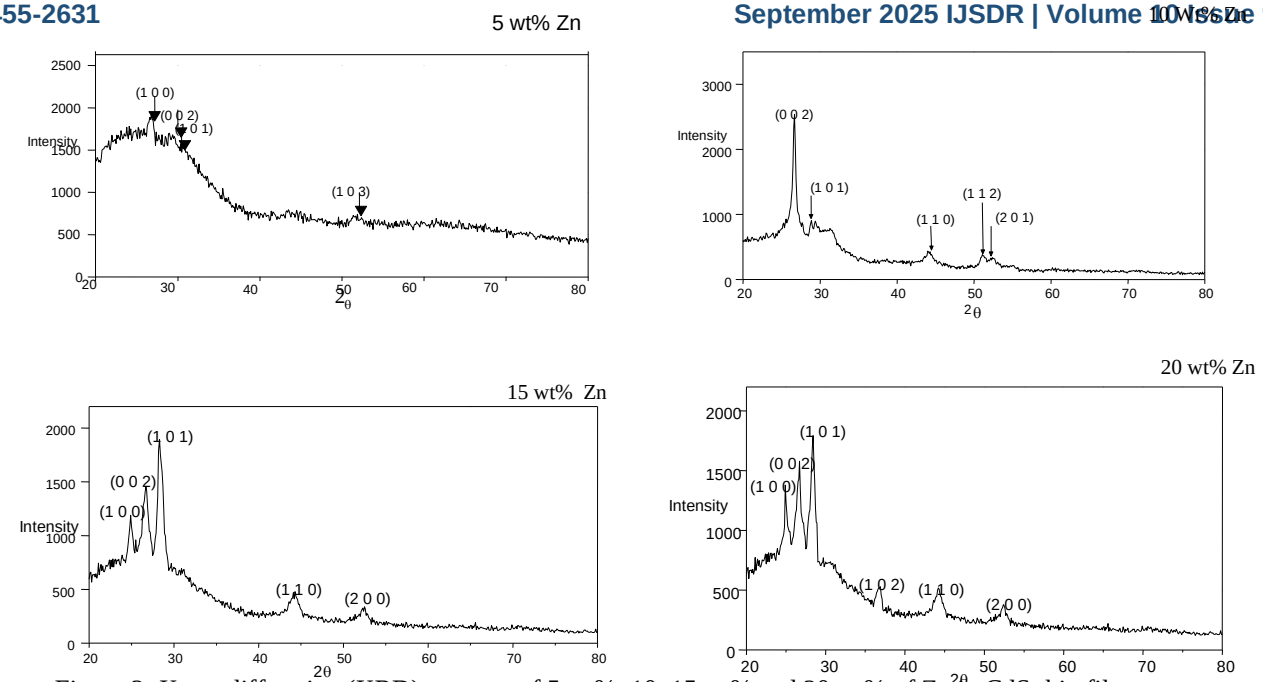

Figure 2: X-ray diffraction (XRD) patterns of 5 wt%, 10, 15 wt% and 20 wt% of Zn in CdS thin films

Table 1 Structural parameters of Zn doped CdS thin films

Doping concentration of Zn (at%)	Thickness of the film (nm)	2θ (°)	FWHM (°)	d-spacing (nm)	Lattice constant, a (nm)	Crystallite size, D (nm)	Number of crystallites per unit area, N ($\times 10^{17}$ m^{-2})	Micro strain, ε ($\times 10^{-3}$ lin^{-2} m^{-2})	Dislocation density, δ ($\times 10^{17}$ lin m^{-2})
5	205	26.70	0.56	0.3327	0.4706	15.24	0.58	1.030	0.4311
10	232	26.75	0.68	0.3303	0.4672	12.55	1.17	1.248	0.6349
15	262	26.82	0.98	0.3290	0.4653	8.71	3.96	1.793	1.3184
20	295	26.96	1.12	0.3265	0.4619	7.62	6.66	2.039	1.722

3.2 Surface morphology Studies:

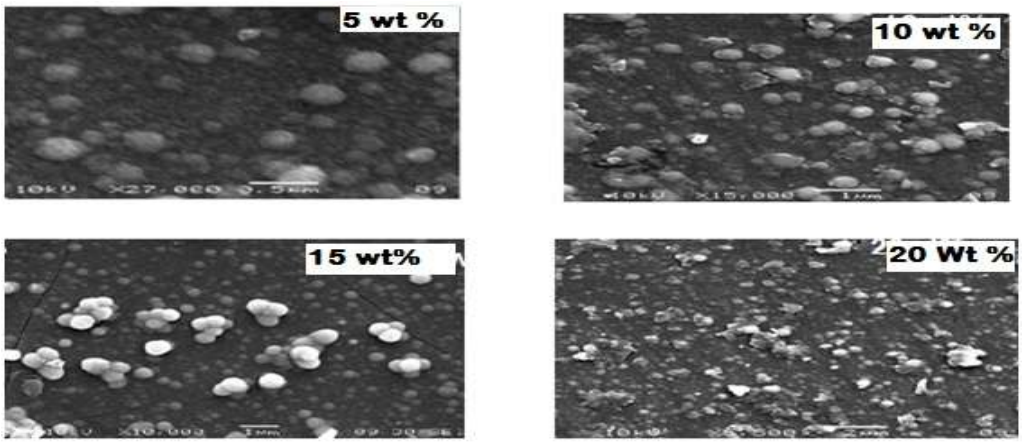

Fig. 3 SEM images of 5%, 10%, 15%, 20% Zn doped CdS thin films

Scanning Electron Microscopy is one of the important tools to know the surface morphology of the films. It is generally used for the topographical studies of the films surface and to know the more information regarding the physical features, growth mechanism, structure, shape and size of grains. Figure 3 shows the SEM photographs of different wt % of Zn doped CdS thin films.

Porosity and clusters of small crystallites are present in certain regions of Zn doped CdS thin films shown in Fig. 3. With the increase of Zn doping from 10 wt% to 20 wt % in CdS thin films the grains are relatively smaller in size and compact distribution is observed over the surface with good attachment between the grains . SEM photographs conforms the decrease in grain size with the increase wt % of Zn content in CdS films as previously reported by Vijay Sanap et.al.[30].

3.3 Compositional analysis with EDAX studies:

An energy dispersive X-ray analysis (EDAX) is used to determine the elemental composition of the films. Figure 4 shows the typical energy dispersive X-ray spectra for 10 wt % Zn-doped CdS thin films. The peaks show the presence of Cd, Zn, and S in the prepared thin films. The atomic percentage of the elements Zn, Cd, and S is provided in Table 2. From Table 2, it can be seen that the weight percentage of sulfur remains almost the same, while the weight percentage of cadmium decreases as the Zn doping percentage increases from 5% to 20%. The elemental composition of the film material is almost the same as that of the initial solution used in the bath.

Table 2 Elemental composition of Zn doped CdS thin films

Doping concentration of Zn (wt%)	Element (wt%)		
	Cd L	S K	Zn K
5	46.18	49.30	4.52
10	43.54	46.65	9.89
15	41.05	44.14	14.89
20	40.13	41.05	19.36

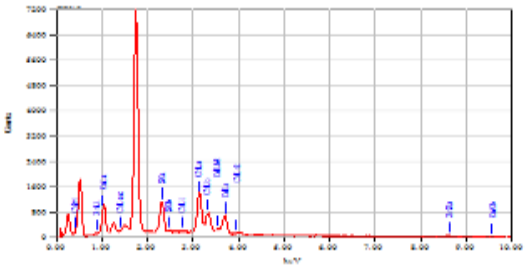

Fig.4.Representative EDAX spectra of 10wt% of Zn doped CdS thin film

3.4 Thermoelectric properties studies:

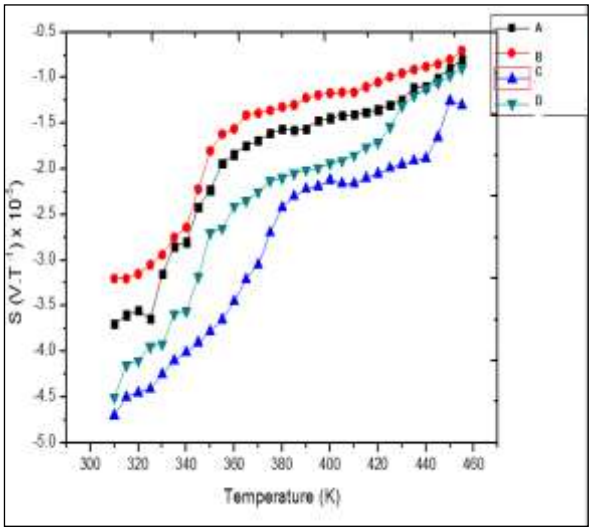

Fig.5. Seebek coefficient as fuction of temperature. (A-5,B-10,C-15 and D-20wt%)

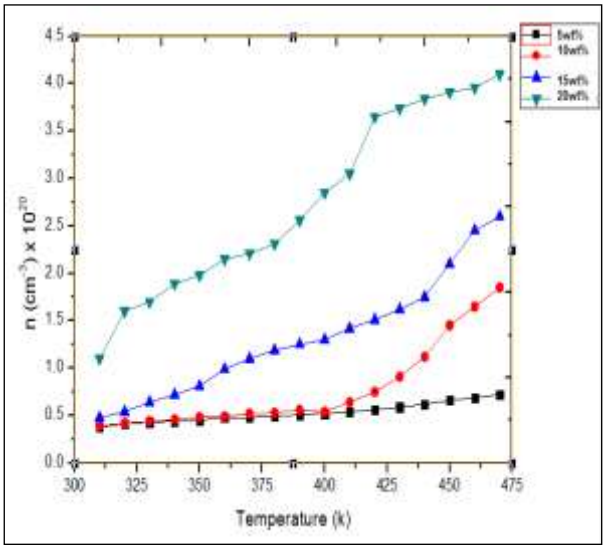

Fig.6. Charge carieer density as function of temperature.

The Seebeck coefficient measures how much voltage is created when there is a temperature difference in a material [31]. It is the ratio of the voltage difference (ΔV) to the temperature difference (ΔT) across the sample, and it is calculated using this equation.

$$S = \Delta V / \Delta T \quad (2)$$

For all the CdZnS thin films, the thermoelectric voltage is negative, which shows that the material is an n-type semiconductor. From Figure 6, we can see that the Seebeck coefficient (S) of Zndoped CdS thin films rises from 3.21×10^{-5} to 4.74×10^{-5} V K^{-1} as Zn content increases. The Seebeck coefficient also goes up with temperature, which is similar to behavior seen in degenerate semiconductors. This matches previous findings about Cu_2SnS_3 thin films by Ketan Lohani et al. [32].The carrier concentration (n) is calculated using this equation [33]

$$S = \left(\frac{8\pi^2 k_B^2}{3eh^2}\right) . m^* T . \left(\frac{\pi}{3n}\right)^{\frac{2}{3}} \quad (3)$$

Here, k_β is the Boltzmann constant (8.61×10^{-5} eV K^{-1}), e is the electron charge, h is the Planck constant (4.135×10^{-15} eV Hz^{-1}), and m* is the effective mass of the charge carriers. The carrier concentration is found by measuring the Seebeck coefficient at different temperatures. It increases from 1.12×10^{19} to 0.32×10^{20} cm^{-3} as Zn content goes from 5 to 20 wt% in CdS thin films at room temperature, as shown in Figure 5. The rise in carrier concentration improves electrical conductivity but lowers the Seebeck coefficient. Figure 6 shows how electrical conductivity (σ) changes with temperature for Zn-doped CdS thin films. As temperature increases, electrical conductivity also increases because more charge carriers are available. Electrical conductivity ranges from 0.12×10^{-5} to 1.11×10^{-5} Ω^{-1} cm^{-1} as Zn concentration increases from 5 to 20 wt%. Thermal conductivity (k) is the sum of lattice thermal conductivity (k_L) and electronic thermal conductivity (k_e). The total thermal conductivity equation is $k = k_e + k_L$. Total thermal conductivity of Zn-doped CdS thin films is calculated using this equation [34]:

$$k = (V \times I \times L) / (\Delta T \times A) \quad (4)$$

Where V × I is the heat power, L is the distance between two thermocouples, ΔT is the temperature difference, and A is the cross-sectional area of the film. Figure 6 shows how total thermal conductivity changes with temperature from 313 to 450 K. Lower thermal conductivity may be because of pores in the thin films. The temperature-dependent thermal conductivity of Zn-doped CdS thin films was measured between 313 and 453 K. As temperature increases, total thermal conductivity decreases, but it goes up with higher Zn content due to phonon scattering at higher temperatures.The electronic thermal conductivity (k_e) of Zn-doped CdS thin films was measured using the Wiedemann–Franz relation [35,36].

$$k_e = L \sigma T \quad (5)$$

Where L = 2.45 × 10^{-8} WΩK^{-2}, σ is the electrical conductivity, and T is the absolute temperature in Kelvin.

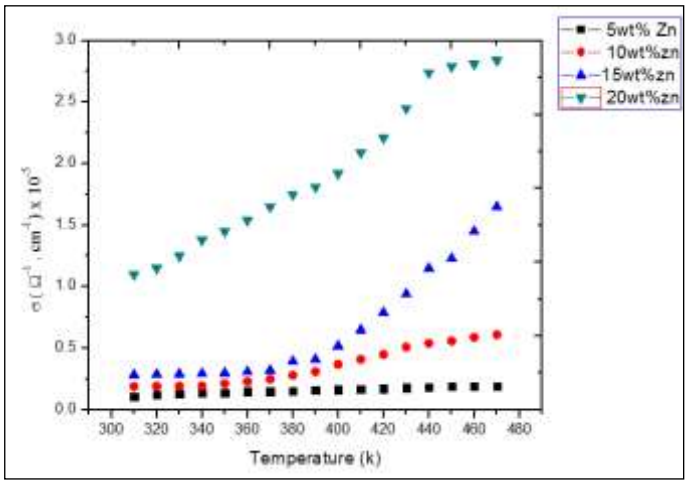

Fig.7 Electrical conductivity as a function of temperature

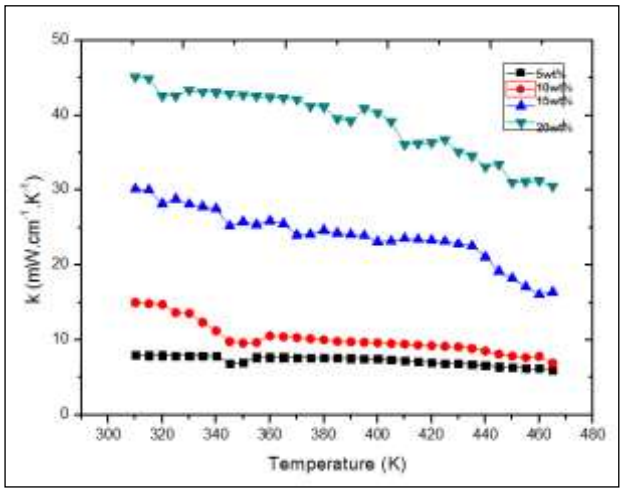

Fig. 8.: Total thermal conductivity as function of temperature : ;

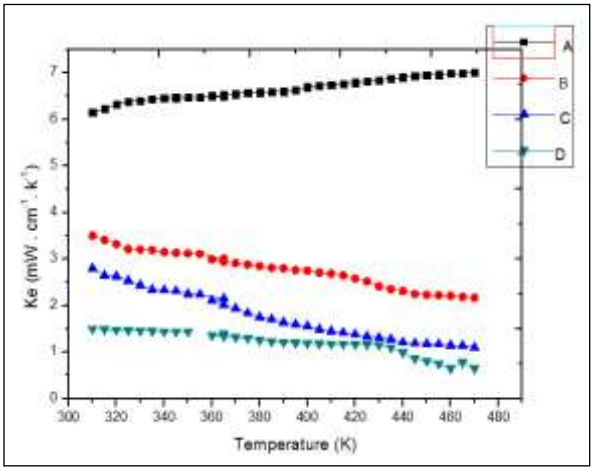

Fig.9 Temperature:as function of electronic thermal conductivity(A-5,B-10,C-15 and D-20wt%)

Figure 9 shows how the electronic thermal conductivity (k_e) of Zn-doped CdS thin films changes with temperature. The electronic thermal conductivity (k_e) slightly decreases as the temperature increases. This is different from what happens in bulk materials. This behavior could be because of phonon boundary scattering, electron-phonon scattering, defects in the thin film material, and impurities in the thin film material [37].

4. Conclusions:

Zinc-doped cadmium sulfide thin films were made using the chemical bath deposition method on clean glass surfaces. The zinc content was changed from 5 to 20 percent by weight. XRD tests showed that the zinc-doped cadmium sulfide films have a hexagonal wurtzite structure. As the zinc content increased, the positions of the diffraction peaks moved to higher angles. The surface structure analysis showed that when zinc doping increased from 10 to 20 percent, the grains in the sample became smaller and more closely packed. The composition of the films was checked using EDAX. The negative Seebeck coefficient values for the zinc-doped films suggest they are n-type semiconductors. The number of charge carriers in these films was between 10^{19} and 10^{20} per cubic centimeter. It was also found that as temperature rose, the electrical conductivity of these films went down. These findings show that the zinc-doped cadmium sulfide thin films, made through chemical bath deposition, could be useful for use in optoelectronic devices.

5.Acknowledgment: Author is very much thankful to Principal S.S.V.P.S. College, Shindkheda for providing laboratory facilities and co-operation to conduct this work.

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