6. ROOM TEMPERATURE OPTICAL AND MAGNETIC PROPERTIES OF (Fe, K) DOPED ZnO THIN FILMS

6.1 INTRODUCTION

Alkali elements are well known materials for tuning ZnO optical and electrical behaviors. Alkali doped ZnO films have been broadly investigated in recent decades. Sung-Kyu Kim et al reported that when K doped ZnO thin films were synthesized on Al₂O₃ (001), the optical properties were improved [161]. Linhua Xu et al. also reported that the optical emission was emerged while K doped ZnO were annealed during different temperatures [96]. Depending on the different types of substrates such as Si (111), ZnO exhibited different emissions such as green and yellow emissions at 529 – 567 nm and 600 – 640 nm due to oxygen vacancy and oxygen interstitials respectively [97]. For Na-doped ZnO, the carrier mobility was 2.1 cm² V⁻¹ S⁻¹ and structural and optical properties were reported elsewhere [162-164]. Li doped ZnO is also used for developing the ferroelectric, optical and multiphonon properties of ZnO semiconductor [165 and 166]. In latest decades, Fe doped ZnO has been synthesized for optical properties [167] because Fe is well known optical emitter in doped ZnO. Y. Zhang et al. reported [168] the optical mechanism of ZnO alloyed with Fe ion. Not only optical properties but Fe is also well known as a doping element for altering the magnetic and electrical properties [169-171]. The extensive literature survey shows that only few works were reported on the optical properties of dual doped ZnO films. Some experimental works such as Al-K [172], Li-N [2], Li-Mg [3], Fe-Co [173] and Fe-N [174] reported the dual doped ZnO to investigate the optical and magnetic properties.

As per the literature till date the study on the optical properties of K and Fe-doped ZnO thin films have not been reported yet. Both Fe and K when doped to ZnO separately, they modify the band gap and also the luminescence characteristics and hence, Fe and K simultaneously doped to ZnO can bring out some interesting results and so in the present study,(K,
Fe) codoped ZnO thin films were investigated for the influence on the optical properties. The optical properties of K doped ZnO films show that 1% of K exhibited better optical properties [150]. For further optical investigation, the transition metal Fe is added into ZnO: K (1%) due to its excellent optical emission property. The chemical bath deposition method was employed to fabricate these films. The influence of Fe concentration on the optical behavior has been discussed in the transmittance and photoluminescence sections. In the present work, 1% K doped ZnO would be indicated as ZnO: K (1%). The main purpose of this study is to examine the effect of Fe ion concentration on optical properties of ZnO: K (1%) films.

6.2 RESULTS AND DISCUSSION

6.2.1 Structural analysis

The XRD pattern of codoped (K, Fe) ZnO thin films are shown in Figure 6.1. All the thin films exhibit hexagonal crystal phase and it is confirmed with standard JCPDS card (PDF # 891397, 890510) number. In XRD pattern, the three prominent peaks such as (100), (002) and (101) were obtained for all films without any secondary phase. In our previous report, three prominent peaks such as (100), (002) and (101) were observed for ZnO: K (1%) thin film [150]. In the present work, when Fe concentration is increased, the crystal properties of the codoped ZnO thin films have changed. The low intensity peak was observed for ZnO: K (1%) [150]. However, in the present work, it is observed that when Fe is introduced, the intensity of three prominent peaks has changed. The variation in intensity indicates the incorporation of Fe ions in the lattice of ZnO site. In the doping process, the three prominent peaks are shifted from higher to lower angles due to the different ionic radius of Fe such as Fe$^{3+}$ and Fe$^{2+}$. For 2, 3 and 4 % of Fe, the three prominent peaks shifted to higher angle than 1 % Fe due to the inclusion of Fe$^{3+}$ (0.068nm) [36]. For 4 % Fe, the (002) peak shift to lower angle due to the high ionic radius (0.078) of Fe$^{2+}$ [175 and 176].
In the entire XRD pattern, the intensity of (002) plane varied for different Fe ion concentrations which indicates that the film has grown along c-axis. In the XRD pattern, the high intensity of (002) plane reveals the improved crystallinity [177]. The full width half maximum of (002) peaks are significantly varied with various Fe concentrations. For 4% Fe, the FWHM is lower than others. Shibu saha et al. reported that the low FWHM reveals the deterioration of the crystallinity [178].

The crystalline sizes of thin films are calculated using Scherrer formula 6.1.

\[
D = \frac{0.9 \lambda}{\beta \cos \theta}
\]  

6.2.2 Surface morphology analysis and EDAX spectrum

The surface morphology of dual doped (K, Fe) ZnO thin films were analyzed by field emission scanning electron microscope (FESEM SUPRA “55”) as shown in Figure. 6.2. SEM image shows that morphology changes with Fe doping concentrations. The film exhibits small grains of varied size at
different level of Fe. So, when Fe ion concentration is increased, the surface morphology of K doped ZnO thin films changed due to the incorporation Fe ion in ZnO lattice site. The presence of chemical elements such as Zn, O, K and Fe is confirmed by Energy dispersive X-ray analysis spectroscopy which is shown in Figure 6.3, the substrate peak is presented between 2.4 to 2.5 eV [150].

Figure 6.2: Surface morphology (FESEM) of (K (1 % ), Fe) codoped ZnO for Fe concentrations: (a) 1 %, (b) 2 %, (c) 3 % and (d) 4 %.
**Figure 6.3**: EDAX spectrum of (K (1%), Fe) codoped ZnO for Fe concentrations: (a) 1%, (b) 2%, (c) 3% and (d) 4%.

### 6.2.3 Surface topography

In Figure 6.4, three dimensional (3D) surface topography of (K, Fe) codoped ZnO thin films are presented. Surface topography was scanned at 5x5 μm in tapping mode. The average roughness and root mean square values were determined. The average roughness are 84.50 nm, 73.06 nm, 69.80 nm and 50.35 nm at level 1, 2, 3 and 4 % Fe respectively. The RMS values are 107.60 nm, 94.14 nm, 86.94 nm and 69.43 nm for 1, 2, 3 and 4 at % Fe respectively. The decrease in average roughness and RMS shows that the crystalline quality of the co-doped ZnO thin films has been improved by increase in Fe concentration. The low roughness indicates the enhancement of crystalline quality [179].
Figure 6.4: Atomic force microscope of (K (1 %), Fe) codoped ZnO for Fe concentrations: (a) 1%, (b) 2%, (c) 3% and (d) 4%.

6.2.4 Transmittance Spectrum and Optical Band Gap

The transmittance spectrum of (K, Fe) codoped ZnO nano films are shown in Figure 6.5. The (K, Fe) codoped ZnO thin films exhibit a low transmittance as seen from Figure 6.5. In the visible region, the transmittance are 50 %, 45 %, 25 % and 10 % for 1, 2, 3 and 4 at % Fe respectively and the transmittance is found to decrease with increase in Fe dopant concentration. The film thickness is one of the main factor for low transmittance. In the doping process, the film thickness are 4.348 μm, 4.690 μm, 5.078 μm and 6.520 μm for 1, 2, 3 and 4 % Fe respectively. Linhua Xu et al. and S. M. Salaken et al. have reported that the optical transmittance obviously reduced in the visible region due to the Fe ion concentrations [176 and 180]. C. S. Prajapati et al. have studied that the low transmittance was obtained for Fe doped ZnO thin films due to lattice defects into ZnO lattice [175]. Due to the film thickness, the incident light is absorbed much
and so the transmittance light intensity is less pronounced. This fact is well reported by the absorption coefficient values of these thin films (Figure.6.10).

![Image of UV transmittance spectrum](image.png)

**Figure. 6.5: UV transmittance spectrum of (K (1%), Fe) codoped ZnO for Fe concentrations: (a) 1 %, (b) 2 %, (c) 3 % and (d) 4 %.

The optical band gap of co-doped (K, Fe) nano ZnO films are calculated from the equations 6.2 and 6.3.

\[
\alpha = \frac{1}{d} \ln \left(\frac{1}{T}\right) \quad (6.2)
\]

\[
(ch\vartheta)^2 = A(h\vartheta - E_g) \quad (6.3)
\]

where, \(\alpha\) is absorption coefficient, \(d\) is film thickness, \(h\vartheta\) is photon energy and \(E_g\) is energy gap. The optical band gaps of co-doped ZnO films are shown in Figure.6.6. The optical energy gap can be obtained by extrapolating the linear part to x axis. In our previous work, the band gap was 3.94 eV for ZnO: K (1%) film [150].
The energy gap reduces due to the increase in Fe doping concentration. The band gap values are 3.42 eV, 3.24 eV, 3.18 eV and 3.06 eV for 1, 2, 3 and 4 at % Fe respectively and this indicates the red shift. C. S. Prajapati et al. reported that when Fe ion was doped with ZnO, the optical band gap changes [175]. However, Linhua Xu et al. reported that the band gap of ZnO was increased by Fe ion concentrations [176]. The red shift was also observed for ZnO thin films due to the high doping material [167], renormalization effect [101] and film thickness [167 and 181]. Among the three factors, the change in the optical band gap also depends on the thickness of the thin film.

### 6.2.5 Optical constants

The refractive index of codoped ZnO films are calculated from equations 6.4 and 6.5.

\[ n = \left( \frac{1+R}{1-R} \right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \]  \hspace{1cm} (6.4)

\[ k = \frac{2\lambda}{n\omega} \]  \hspace{1cm} (6.5)
where \( R \) is reflectance, \( n \) is refractive index, \( k \) is extinction coefficient, \( \alpha \) is absorption coefficient and \( \lambda \) is wavelength. The refractive index of codoped ZnO thin films as function of wavelength is shown in Figure 6.7. The refractive index varies with variation in Fe concentrations. In the visible region the light is normally dispersed due to the contribution of virtual electronic transition [182] and lower dense medium.

![Graphs showing refractive index and extinction coefficient for different Fe concentrations](image)

**Figure. 6.7:** Refractive index of (K (1%), Fe) codoped ZnO for Fe concentrations: (a) 1 %, (b) 2 %, (c) 3 %, and (d) 4 %.

For the 375 nm, the refractive index of co-doped ZnO thin films are 5.3, 3.2, 4.3 and 6.2 for 1, 2, 3 and 4 % Fe respectively. The thin films are exhibits significant changes and also suitable for integrated optical device application. The normal dispersion indicates that the films do not have voids and any defects. The lower values of extinction coefficient indicate that film is well smoothness.
Figure 6.8: Dielectric constant of (a) K(1%) - Fe(1%)-ZnO, (b) K (1%)- Fe (2%)-ZnO, (c) K(1%) – Fe (3%) – ZnO and (d) K (1%)- Fe (4%)-ZnO.

In Figure 6.8 shows the real ($\varepsilon_r$) and imaginary ($\varepsilon_i$) parts of dielectric constant of codoped (K, Fe) ZnO films are determined using the equations 6.6 and 6.7.

\[\varepsilon_r = n^2 - k^2\]  
\[\varepsilon_i = 2nk\]  

Commonly, the real and imaginary parts of dielectric constant is similar to refractive index because of the absolute refractive index is corresponding to dielectric constant. The real part of dielectric constant decreases with increasing wavelength in the visible region and increases in UV region similarly refractive index. The changes of real part of dielectric constant values are indicating the interaction between photons and electrons [4, 183].

Figure 6.9 shows the variation of optical band gap, refractive index and extinction coefficient of Fe concentrations. In Figure (a), the optical band gap decreases significantly with increases in Fe concentrations. Figure (b) shows
the refractive index of codoped ZnO films is increased (at $\lambda = 375$ nm) considerably for different doping (Fe) concentrations. This is indicates that the light is normally travelled through the medium. Moreover, the extinction coefficient ($k$) reveals that the well smoothness of thin films surface.

Figure. 6.9: The figure shows (a) band gap versus different Fe % and (b) refractive index and extinction coefficient versus different Fe %.

Figure.6.10 shows, the absorption coefficient ($\alpha$) of (K, Fe) co-doped ZnO thin films for different of Fe doping concentrations. For ZnO: K (1%), $\alpha$ was $2.75 \times 10^5$ cm$^{-1}$ [150].

Figure. 6.10: Absorption coefficient of (K (1 %), Fe) codoped ZnO for Fe concentrations: (a) 1 %, (b) 2 %, (c) 3 % and (d) 4 %.
In the UV region at $\lambda = 375\text{nm}$, absorption coefficient are $2.03 \times 10^5 \text{ cm}^{-1}, 2.48 \times 10^5 \text{ cm}^{-1}, 3.30 \times 10^5 \text{ cm}^{-1}$ and $3.95 \times 10^5 \text{ cm}^{-1}$ for 1, 2, 3 and 4 % of Fe respectively. In the present investigation, in the UV region, the absorption of light depends on the thickness of the film. The higher absorption of ZnO thin films are suitable for anti-reflecting coating (ARC) and optoelectronic applications [184].

6.2.6 Photoluminescence study

Figure 6.11 shows the photoluminescence spectrum of (K, Fe) codoped ZnO films at room temperature. Generally, UV emissions exist in the range between 360 nm to 380 nm range [185]. The UV emission was observed at 389 nm for ZnO: K (1%) [150].

![Photoluminescence spectrum](image)

**Figure. 6.11: Photoluminescence spectrum of (K (1 %), Fe) codoped ZnO for Fe concentrations: (a) 1 %, (b) 2 %, (c) 3 %, and (d) 4 %.**

In the PL spectrum, UV emission appears around 345 nm (3.59 eV) due to the free exciton transition [59]. However, in the photoluminescence spectrum, the intensity of UV emission is significantly varies for 1, 2 and 3 % of Fe ion concentrations but the UV intensity is reduced for 4 % Fe ion concentration.
This may be due to the low concentration of Zn and O and it can be seen in EDAX spectrum. This is the evidence for the variation of UV intensity in the photoluminescence.

The weak blue emission is presented with low intensity at 437 nm due to the low interstitial of Zn [186]. The red emission is obtained between in the range of 661 nm to 663 nm due to the surplus of oxygen or interstitials of oxygen [187]. The peak position of the photoluminescence depends on the contribution between the free exciton and transition between free electrons to acceptor bound holes [188]. And also the position and intensity of UV and red emissions in PL are enhanced by incorporation of Fe ion in ZnO lattice site. In this study photoluminescence spectrum clearly reveals that the co-doped ZnO thin films are free from any defects.

6.2.7 Magnetic properties

Figure.6.12 shows the magnetic hysteresis (M-H) curve measured at room temperature for the prepared thin film samples of ZnO:K, ZnO:K, Fe (1 %) and ZnO:K, Fe (4 %). All the films exhibited typical ferromagnetic hysteresis loop at room temperature.

![Magnetic Hysteresis Curve](image)

**Figure. 6.12:** Room Temperature M-H curves of ZnO: (K 1 %), (K, Fe 1 %) and (K, Fe 4 %) doped ZnO thin films.
When the Fe is doped to ZnO along with the K which is an alkali metal, a significant change has occurred in the FM loop and this indicates that Fe has influenced the FM character of the thin films. When K and Fe doped ZnO thin films are considered, the magnetic saturation ($M_s$) and magnetic retentivity ($M_r$) are found to increase with the increase in the Fe concentration. However, the coercivity ($H_c$) decreases with the Fe dopant level. Low coercivity and high saturation magnetization is required for spintronics memory devices and this is obtained for the ZnO: K, Fe (4 %) thin films compared to the other thin films.

Table 6.1 shows the magnetic saturation ($M_s$), magnetic retentivity ($M_r$) and coercivity ($H_c$) for all the thin films. The ferromagnetic nature of K doped ZnO is due to the shallow acceptor created. Hyeoun Jun lee et al reported that the alkali elements created the shallow acceptor (p-type) above the valence band and it has indicated that the p-type elements [189] induce the ferromagnetism in doped ZnO. Due to the cationic effect of Li/Na/K, the shallow acceptor level will create the holes in ZnO lattice. When the holes are created in alkali doped ZnO, the magnetic moment will appear [155].

Table 6.1 Magnetic parameters of ZnO: K, ZnO: (K, Fe 1%) and ZnO: (K, Fe 4%) thin films.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Saturation Magnetization ($M_s$) in emu/cm$^3$</th>
<th>Retentivity ($M_r$) in emu/cm$^3$</th>
<th>Coercivity ($H_c$) in Oe</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO: K</td>
<td>36.26</td>
<td>14.75</td>
<td>439</td>
</tr>
<tr>
<td>ZnO: (K, Fe 1%)</td>
<td>15.42</td>
<td>16.10</td>
<td>630</td>
</tr>
<tr>
<td>ZnO: (K, Fe 4%)</td>
<td>46.67</td>
<td>20.11</td>
<td>468</td>
</tr>
</tbody>
</table>

Low coercivity of Fe doped samples speculates that these films are soft compared to ZnO: K thin film. This indicates that Fe along with K in ZnO give a soft FM nature and this will be useful for suitable applications.
Several reasons were given in the earlier studies for the existence of ferromagnetism in Fe doped ZnO. An earlier report claims that Fe cluster and secondary formation (Fe$_2$O$_3$, Fe$_3$O$_4$) were responsible for origin of ferromagnetism in Fe-doped ZnO [190]. Xiaojuan Wu et al. [191] reported that the origin of ferromagnetism in Fe doped ZnO is due to interaction between local spin-polarized electrons and this interaction is occurred by exchange of Fe$^{3+}$ ions.

It is known that the defects in ZnO have the effect of changing its band gap and the concentration of charge carriers. In the present study, the incorporation of K to ZnO host lattice and the incorporation of (K, Fe) to ZnO reveal the possible defects through the respective PL. There is no noticeable change in the PL peak shift. However, there is a change in the intensity of the peaks.

From the PL of ZnO: K (Figure 6.11), it is clear that there are no defect levels corresponding to oxygen vacancies ($V_o$) as there is no green emission [190] and the PL consists of the ultraviolet emission centered at 389 nm. For comparison, PL for ZnO is also given which shows the existence of blue emission corresponding to Zinc interstitials (Zn$_i$) [192 and 96] depicting the n-type nature of ZnO. However, when K is incorporated into ZnO, it is seen that the intensity of blue emission abruptly decreases. This indicates the disappearance of the Zn$_i$ which are hole killers [154] and so the decrease in Zn$_i$ indicates that more holes tend to exist and hence the magnetization in ZnO: K is hole mediated [69]. ZnO:K introduces more holes in the ZnO lattice when Zn is replaced by K as K forms the shallow acceptor levels as in the case of Li doped ZnO [69,193 and 194].

When Fe is added to ZnO: K, a significant change in the PL spectra is seen. The blue emission appeared for ZnO: K, now has almost disappeared and shows a very feeble contribution around 450 nm which means that Fe introduction has greatly reduced the formation Zn$_i$ defects further. There are two main emission peaks observed. The one centered about 345 nm to 350 nm corresponds to strong UV emission of ZnO which is due to the exciton recombination corresponding to the near band edge exciton emission and the
other one is weak red emission centered about 675nm. No emission corresponding to other defects such as V_o and V_{zn} are seen. When Fe is doped to ZnO, the hybridization between O–p states and TM –d states leads to ferromagnetism nature [156]. Also, According to the Ruderman–Kittel–Kasuya–Yosida (RKKY) theory [158 and 159], the exchange interaction between local spin-polarized electrons of Fe^{2+} ions and conductive electrons is the another reason that leads to the ferromagnetism. The variation in the optical band gap in doped ZnO indicates the variation in carrier concentration and it corresponds to changes in the magnetic properties.

6.3 CONCLUSION

K doped and (K and Fe) doped ZnO DMS thin films were fabricated by chemical bath deposition method. Hexagonal crystal structure was confirmed by X-ray diffractometer for all the doped thin films. Band gap decreases with Fe concentration indicating the red shift. Typical FM character is exhibited by all the doped thin films at room temperature. Magnetization is found to be enhanced with the Fe concentration. Fe doped samples exhibit soft FM nature. The absence of secondary phases in the XRD pattern and the insignificant defect level shows that the magnetism in the doped ZnO thin film is not due to these two reasons and it is mainly due to p-d hybridization as revealed by the band gap which is dependent on the p-d hybridization. The different optical properties such as refractive index and absorption coefficient revealed that the optical behavior of thin films and the low extinction coefficient value indicates the better quality of the film. The absorption coefficients show an increase with doping concentration. The photoluminescence spectrum revealed that the co-doped ZnO thin films are mostly defect free. The present investigation confirms that K and Fe simultaneously doped ZnO thin films are diluted magnetic semiconductors at room temperature due to the magnetic and semiconducting nature of these thin films. Hence, these Fe and K simultaneously doped ZnO thin films are potential candidates for DMS applications, anti-reflecting coating (ARC) and optoelectronic devices.