Chapter 2

Growth and Characterization of Cd$_{1-x}$Cr$_x$Te Dilute Magnetic Semiconducting Crystals

2.1 INTRODUCTION

For the past two decades extensive studies were carried out on II-VI, III-V and IV-VI DMS compounds for room temperature ferromagnetism (Haury et al., 1997; Ohno et al., 1991). It is fascinating to see that the transition metals find greater solubility in II-VI compound semiconductors, when compared with other compound semiconductors. It is easier to incorporate magnetic ions with +2 oxidation state in the host lattice of II-VI compound DMS such as ZnTe, ZnSe, CdSe and CdTe (Furdyna 1982). Ferromagnetism was observed, when the transition metal such as Cr was doped into II-VI semiconductors (Ando et al., 2001). Cr metal ion plays a dual character by creating a hole carrier as well as a ferromagnetic impurity in the host semiconductor (Guo et al., 2006) and reported that super exchange interaction between the Cr$^{2+}$ ions was responsible for the origin of ferromagnetism in Cr doped II-VI semiconductors. Till to date, less work had been reported on Cr doped II-VI DMS. Among the II-VI semiconductors, CdTe with a band gap of 1.45 eV is a promising candidate as host material for DMS. Recently, theoretical predictions confirmed the half metallic ferromagnetism in Cr doped CdTe crystals (Noor et al., 2011). Few researchers (Ko and Blamire, 2006) had made attempts for room temperature ferromagnetism in Cr doped CdTe crystals. Since reports on Cr doped CdTe crystals are meager, a systematic investigation on room temperature ferromagnetism with compositional dependence is required. This chapter reports the synthesis of Cd$_{1-x}$Cr$_x$Te crystals grown by vapor phase technique. Further, the effect of Cr concentration on structural, optical, dielectric and magnetic properties of Cr doped CdTe crystals was also envisaged.

2.2 EXPERIMENTAL

Cd$_{1-x}$Cr$_x$Te crystals with different Cr concentrations (0 ≤ x ≤ 0.5) were grown from pure CdTe and CrTe by modified vapour phase growth technique (Chandrasekharan et al., 1983). CdTe and CrTe (99.99% M/S Sigma Aldrich) were taken as source materials. CrTe in cubic phase was prepared freshly. Stoichiometric
quantities of CdTe and CrTe were mixed and ground thoroughly using Agate mortar and pestle for 12 hours. The mixture was sintered at 500°C in a quartz tube under a pressure of $2 \times 10^{-3}$ mbar for 12 hours and cooled slowly to room temperature. This sintered material was ground again for 6 hours and used as a charge for the growth of $\text{Cd}_{1-x}\text{Cr}_x\text{Te}$ crystals. The ground charge was then loaded to a well cleaned quartz tube and the opening end was drawn into a fine capillary of 20 cm length leaving a space of 10 cm from charge for growth of the crystal. The growth tube was carefully introduced into a well cleaned protective quartz tube and evacuated to a pressure of $2\times10^{-3}$ mbar. The entire set up was placed in a programmable horizontal furnace such that the charge was kept at the highest temperature zone. The temperature of the furnace was slowly raised to 980 °C at a rate of 20 °C per hour and maintained at 980 °C for 48 hours before cooling it to room temperature. Each growth run lasted for 5 to 6 days. The growth tube was carefully removed from the furnace and the crystal boules were taken out by gently breaking the growth tube. The optimum growth conditions for growing the Cr doped CdTe crystals were arrived through trial and error method. Good quality crystals of 1 cm to 2 cm long were grown in the present work and the photographs of the grown crystals are shown in Fig. 2.1. The grown crystals were subjected to structural, morphological, optical, dielectric and magnetic characterizations.

Fig. 2.1 Photograph of $\text{Cd}_{1-x}\text{Cr}_x\text{Te}$ grown single crystals at $x=0.00, 0.01, 0.03$ and $0.05$

2.2.1 CHARACTERIZATION

Crystal planes of the grown crystals were recorded using XRD (Bruker, D8 Advance diffractometer) equipped with Ni filter and operated at 40 kV, 30 mA ($\text{CuK}_\alpha$ radiation, $\lambda = 0.15406$ nm) with a scan speed of 0.02 °s$^{-1}$ in the $2\theta$ range of 20° – 80°. The composition and surface morphology of the samples were determined by EDAX.
instrument (Genesis X4M) and scanning electron microscope (SEM JSM 840A). The room temperature diffuse reflectance spectra of the samples were recorded using double beam UV-Vis-NIR spectrophotometer (Jasco V-670) in the wavelength range of 200 nm - 2500 nm. Magnetic studies were carried out using Vibrating sample magnetometer (Lakeshore 7410) with an applied field of 15,000 G. The dielectric properties such as dielectric constant, dielectric loss and ac conductivity were studied in the frequency range of 50 Hz - 100 KHz by varying the temperature in the range of 303 K - 553 K using PSM 1735 impedance analyzer.

2.3 RESULTS AND DISCUSSION
2.3.1 STRUCTURAL STUDIES

Fig. 2.2 X-Ray diffraction patterns of Cd$_{1-x}$Cr$_x$Te single crystals with different Cr concentrations

Fig. 2.2 shows the XRD patterns of Cd$_{1-x}$Cr$_x$Te crystals with different Cr concentrations (x=0.00, 0.01, 0.03 and 0.05). All the XRD patterns coincided with zinc blende structure with (1 1 1) as predominant orientation. All the diffraction peaks were indexed to (h,k,l) miller planes using JCPDS data (89-3053). A gradual shift in the diffraction angle of the XRD peaks towards higher angles was observed with
increase of Cr doping levels. No traces of secondary phases and/or impurities were observed in the XRD patterns. The lattice constant of the $\text{Cd}_{1-x}\text{Cr}_x\text{Te}$ crystals was calculated and found to decrease linearly with increase of Cr doping concentration ($x$) obeying Vegard's law as shown in Fig. 2.3. The reduction in lattice constant with Cr doping concentration may be due to smaller atomic radius of Cr (0.125 nm) than that of atomic radius of Cd (0.158 nm). The decrease in lattice constant may also be due to strain developed in the host CdTe on doping with the dopant species into the host lattice. Similar decrease in lattice constant was also reported in $\text{Cd}_{1-x}\text{Fe}_x\text{Te}$ crystals (Subrahmanyam et al., 2011).

![Graph showing variation of lattice parameter with Cr composition](image)

**Fig. 2.3** Variation of lattice parameter of $\text{Cd}_{1-x}\text{Cr}_x\text{Te}$ single crystals with Cr composition ($x$)

### 2.3.2 SURFACE MORPHOLOGY AND COMPOSITION ANALYSIS

Fig. 2.4 (a) shows typical surface morphology of $\text{Cd}_{0.99}\text{Cr}_{0.01}\text{Te}$ single crystal. It was observed that the surface was smooth without any voids and pits. The existence of the growth layers might be due to unavoidable surface tension and interaction between the surface atoms (Subrahmanyam et al., 2011). No reports are available on the growth patterns of Cr doped CdTe single crystal. Chandrasekharan et al., (1983) have reported that the growth of ZnSe-CdTe crystals was due to active participation.
of screw dislocations associated with crystal anisotropy. Similar growth mechanism is expected in the present system as it is also a CdTe based crystal. Hence, it could be inferred that this growth layers may have the origin and proliferation at and around screw dislocations coupled with the crystal anisotropy. Similar kind of ordered structures in the as grown bulk CdTe compound was reported by (Singh et al., 2010).

The Selected Area Electron Diffraction (SAED) pattern of \( \text{Cd}_{0.99}\text{Cr}_{0.01}\text{Te} \) single crystal is shown in Fig. 2.4 (b). Electron diffraction studies confirmed that the grown \( \text{Cd}_{1-x}\text{Cr}_x\text{Te} \) crystals are single crystalline in nature. Fig. 2.4 (c) shows EDAX spectrum of \( \text{Cd}_{0.99}\text{Cr}_{0.01}\text{Te} \) crystal showing the atomic percentage of Cd:Te:Cr as 49.97 at.% : 49.02 at.% : 1.01 at.% respectively. This confirms that the grown crystals are nearly stoichiometric with the target material.

Fig. 2.4 (a) HRSEM image (b) SAED pattern and (c) EDAX spectrum of \( \text{Cd}_{0.99}\text{Cr}_{0.01}\text{Te} \) single crystal
2.3.3 MAGNETIC STUDIES

Fig. 2.5 (a-d) M-H curves of Cd$_{1-x}$Cr$_x$Te crystals

Fig. 2.5 (a-d) shows the magnetic field dependence magnetization (M-H curves) of Cd$_{1-x}$Cr$_x$Te crystals measured at 300 K using vibrating sample magnetometer. The hysteresis loops observed in the present study display the characteristics of a soft magnetic material. Pure CdTe is diamagnetic in nature as shown in Fig. 2.5 (a). Hence its magnetic susceptibility is negative and ferromagnetism was not expected in it. Whereas, a complete ferromagnetic behavior was observed in all Cd$_{1-x}$Cr$_x$Te crystals with $x=0.01$, 0.03 and 0.05. It can be interpreted that the above room temperature ferromagnetic behavior would arise from the creation of a spin-split impurity band at the Fermi level, i.e. below the conduction band due to the hybridization between the charge carriers of Cr and Cd atoms. Hence, the observed ferromagnetism may be due to super exchange interaction between
localized ‘d’ spins of the Cr\(^{2+}\) ions and the free localized ‘d’ carriers (Mac et al., 1994). Possibility of induced extrinsic ferromagnetism due to Cr ions is not possible here, as Cr ions are antiferromagnetic in nature (Philip et al., 2006). It is quite obvious from the Fig. 5 (b-d) that the Cr doped CdTe crystals show a systematic change in the magnetic behavior with increase in chromium content. This magnetic behavior depends strongly on Cr content. The observed values of magnetization (M\(_s\)) for \(x = 0.01, 0.03\) and 0.05 were 0.0538 emu/g, 0.0032 emu/g and 0.0014 emu/g respectively. It can be seen that as the Cr level increased from \(x=0.01\) to 0.05, a decrease in magnetic moment was observed. The decrease in magnetic moment and weakening of ferromagnetic behavior may be due to the fact that the excess Cr ions may occupy the interstitial positions. This would result in reduction of the ferromagnetic exchange interaction as intrinsic Cr is antiferromagnetic in nature. This kind of behavior is analogous to Cr doped ZnTe system in bulk form (Krishnaiah et al., 2008) and in ZnCrTe thin films (Soundararajan et al., 2011). Hence, it can be concluded that, the ferromagnetic behavior does not originate from any other phases, but it is attributed solely due to the substitution of magnetic ions (Cr\(^{2+}\)) for Cd\(^{2+}\) in the host CdTe crystal.

### 2.3.4 OPTICAL STUDIES

Fig. 2.6 shows the diffused reflectance spectra of Cd\(_{1-x}\)Cr\(_x\)Te (\(x=0.00, 0.01, 0.03, 0.05\)) crystals in the photon energy range of 1.25 eV - 6 eV. The reflectance spectra recorded in the present study was a result of band to band transition and was only due to an allowed direct transition from the top of valence band to the bottom of the conduction band at the centre of the Brillouin zone. From the inset of Fig. 2.6, it was observed that the fundamental absorption edge (E\(_0\)) shifts systematically at the IR region towards lower energies (longer wavelength) with increase of Cr doping level. In the present study it is fascinating to observe E\(_0\)+\(\Delta_0\) peak in the reflectance spectra. The well-defined peaks observed in the energy range of 3–6 eV are due to E\(_0\)+\(\Delta_0\), E\(_1\), E\(_1\)+\(\Delta_1\) and E\(_2\) transitions. The fundamental absorption edge E\(_0\), is a direct allowed transition between the top of valence band \(\Gamma_{15}\) and the bottom of conduction band \(\Gamma_1\) (Cardona and Greenaway, 1963; Enloe et al., 1987; Chadi et al., 1972). The E\(_1\) and E\(_1\)+\(\Delta_1\) peaks result due to transitions from the spin – orbit split valence band \(\Lambda_3\) to the \(\Lambda_1\) conduction band. The E\(_2\) peak is due to transition from X\(_5\) valence band to the X\(_1\) conduction band. In view of the similarity observed between the diffused reflectance
Fig. 2.6 Diffused reflectance spectra of pure and \( \text{Cd}_{1-x}\text{Cr}_x\text{Te} \) crystals (Inset: magnified view of fundamental band edge \( E_0 \) in the photon energy range of 1 eV – 2 eV)

Fig. 2.7 Variation of optical band gap of \( \text{Cd}_{1-x}\text{Cr}_x\text{Te} \) crystals with Cr concentration
spectra of pure CdTe and Cr doped CdTe crystals as shown in Fig. 2.6, it is obvious that the presence of Cr$^{2+}$ ions does not change the energy bands structure. Furthermore, the band gaps calculated from the spectra decreases linearly with increase in Cr concentration ($x$) as shown in Fig. 2.7. The incorporation of Cr$^{2+}$ ions in the system might lead to defects. Addition of impurities could result in increase of pressure at the grain boundaries (Lines and Glass, 1977). Therefore, it can be speculated that the substitution of Cr$^{2+}$ ions for the Cd$^{2+}$ ions could alter the centers of the conduction and valence bands due to which decrease in the band gap of the Cd$_{1-x}$Cr$_x$Te crystals was observed.

### 2.3.5 DIELECTRIC STUDIES

The influence of temperature on the dielectric constant ($\varepsilon'$) and dielectric loss ($\tan \delta$) of the Cd$_{1-x}$Cr$_x$Te crystals in the frequency range 50 Hz – 100 KHz are shown in Fig 2.8 and Fig 2.9. It is clear from these figures that the increase of $\varepsilon'$ and $\tan \delta$ is high for lower frequency and decreased at higher frequency with corresponding increase in temperature for all compositions. These results can be well explained using polarization mechanisms like electronic, ionic, dipolar and space-charge polarizations (Mei et al., 1995). The space charge polarization and dipolar polarization play the most significant role at low frequencies. Both of these polarizations are temperature dependent (Jagdish et al., 2011). In the space charge polarization, when the electric field is applied, the space charges are moved and dipole moments are created leading to accumulation of charges at the grain boundary. Further, these dipole moments are rotated by the applied field giving rise to rotational polarization promoting to high values of dielectric constant. In addition to that whenever there is an increase in the temperature, the charge carriers are thermally activated and their mobility is drifted, which further increases the exchange interaction between electrons resulting an increase in dielectric constant (Amit Kumar et al., 2007). Hence, at lower frequencies, the space charge polarization is more prominent for an increased dielectric constant with the temperature (Azhagushanmugam et al., 2012). Whereas at higher frequencies, the electronic and ionic polarization play a crucial role and it is not temperature dependent. When the charge carriers move, the dielectric constant falls to a smaller value before the field reversal occurs. As the frequency of electric charge carriers are not able to track the
alternation of ac electric field applied beyond a certain critical frequency (Ponpandian et al., 2002), the dielectric constant decreases at higher frequencies. The very low value of dielectric constant at higher frequencies is required for the preparation of materials for ferroelectric, photonic and optoelectronic devices.

Fig. 2.8. Temperature dependence of dielectric constant of pure and Cr doped CdTe single crystal at different frequencies

The frequency dependence of dielectric constant ($\varepsilon'$), dielectric loss (tan $\delta$) and imaginary dielectric constant ($\varepsilon''$) at different temperatures are shown in Fig. 2.10, 2.11 and 2.12. It is observed from these figures that at lower frequency region the $\varepsilon'$ (Fig. 2.10), tan $\delta$ (Fig. 2.11) and $\varepsilon''$ (Fig. 2.12) was found to be high, whereas at higher frequencies it decreased gradually.
This decrease of $\varepsilon'$, tan$\delta$ and $\varepsilon''$ with increasing frequency ($f$) happens when the hopping frequency of the electron exchange between charge carriers might not be able to follow the alternating frequency of applied ac electric field beyond a certain critical frequency (Murthy and Sobhanadri, 1976). Fig 2.13 shows the variation of ac conductivity $\sigma_{ac}$ with temperature. $\sigma_{ac}$ was calculated using the relation

$$\sigma_{ac} = \sigma_0 \exp \left( -\frac{E_a}{k_B T} \right)$$  \hspace{1cm} (2.1)$$

where $\sigma_0$ is a constant, $E_a$ is the activation energy, $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. The activation energies were calculated from the plot of log conductivity against reciprocal temperature at various frequencies as shown in Table 2.1. It is observed that the activation energies are found to decrease with
increase in Cr concentration. But the decrease of activation with ‘x’ is not uniform. This could be due to different defect structures in samples.

Fig 2.10 Frequency dependance of dielectric constant of pure and Cr doped CdTe single crystals at different temperatures

Table 2.1: Summary of activation energy with Cr concentration (x) at different frequencies

<table>
<thead>
<tr>
<th>Cr Concentration ‘x’</th>
<th>E_a in eV for the temperature 303 K - 553 K for different frequencies</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50 Hz</td>
</tr>
<tr>
<td>0.00</td>
<td>1.76</td>
</tr>
<tr>
<td>0.01</td>
<td>1.72</td>
</tr>
<tr>
<td>0.03</td>
<td>1.55</td>
</tr>
<tr>
<td>0.05</td>
<td>1.58</td>
</tr>
</tbody>
</table>
Fig 2.11. Frequency dependance of dielectric loss of pure and Cr doped CdTe single crystals at different temperatures

For lower frequencies, the ionic conduction is characterized by low mobility (i.e. low conductivity) leading to high activation energies, but at higher frequencies electronic conduction is associated with relatively higher mobilities (i.e. high conductivity) and hence it results in lower activation energy (Jonscher 1967). This can be concluded in such a way that the grain boundaries of lower conductivity were found to be effective at lower frequencies while grains of high conductivity are effective at higher frequencies (Kumar and Srivastava, 1994; Koops 1953; Prakash and Baijal, 1985; Smit and Wijn, 1959; Isamael et al., 1995).
Fig. 2.12 Frequency dependence of imaginary dielectric constant of pure and Cr doped CdTe single crystals at different temperatures

Fig. 2.13 Arrhenius plots of ac conductivity of pure and Cr doped CdTe single crystals at different temperatures
2.4 CONCLUSION

Cd$_{1-x}$Cr$_x$Te single crystals were grown by modified vapour phase technique with different Cr doping levels ($x$=0.01, 0.03 and 0.05). The XRD patterns confirmed zinc blende structure of the Cd$_{1-x}$Cr$_x$Te grown crystals. The lattice parameter decreased linearly with increase of Cr content. Morphological studies showed layered structures with no voids and pits on the surface. The magnetization measurements of Cd$_{1-x}$Cr$_x$Te crystals exhibited clear hysteresis loop confirming room temperature ferromagnetism in all the doped crystals. With increase of Cr concentration, the magnetic moment was found to decrease. From the diffused reflectance spectra a shift in the fundamental absorption edge toward higher wavelength $\lambda$ was observed. The band gap decreased with the increase in Cr concentration. The dielectric constant ($\varepsilon'$) and dielectric loss (tan $\delta$) decreased with the frequency of external electric field and increased with the increase of temperature. The ac conductivity was found to increase with an increase in temperature. In perspective to the origin of the ferromagnetism, coupling with XRD, optical and magnetic studies, it was concluded that ferromagnetism arised from the exchange interaction between Cr$^{2+}$ ions and the Cd$^{2+}$ ions in the CdTe host lattice.

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