5.0 INTRODUCTION

The possibility of using electron spins in electronic devices known as Spintronic devices has attracted a growing interest in Diluted Magnetic Semiconductors (DMS). The ferromagnetic DMS can be used in spintronic devices as an effective source of spin polarized electrons. The ferromagnetic materials operating at room temperature with high thermal equilibrium would be a breakthrough in realizing spin-polarized transistors on integrating spin-logic and non-volatile spin memory into the exciting field of quantum computing. Recently, (Zn, Cr)Te thin films with high Cr concentration (20%) was found to exhibit ferromagnetism with a $T_c$ of 300 K. Ferromagnetism in bulk (Zn, Cr)Te has also been found with a $T_c$ of 365 K. This current uniqueness of (Zn, Cr)Te makes it a system of exceptional importance for both basic and applied researches in the field of spintronics. Inspite of this, no systematic investigations on the preparation and characterization on this system has been attempted in particular in bulk form. This motivated the present author to select Zn$_{1-x}$Cr$_x$Te for the present study. Single crystals of Zn$_{1-x}$Cr$_x$Te with $x = 0.001, 0.002, 0.003, 0.004$ and $0.005$ were grown by Vapour phase and Bridgman growth techniques. The as-grown crystals were characterized by EDAX for chemical analysis, SEM for microstructure, XRD for structural analysis, Microhardness by Vicker's method, Optical transitions by diffuse reflectance, magnetic studies by EPR and VSM and charge transport by electrical studies. The results of these investigations and conclusions arrived at are presented in this chapter briefly.

5.1 PREPARATION OF Zn$_{1-x}$Cr$_x$Te SINGLE CRYSTALS

Vapour phase and Bridgman growth techniques are used for the synthesis of Zn$_{1-x}$Cr$_x$Te single crystals with $x = 0.001, 0.002, 0.003, 0.004$ and $0.005$. The optimum growth conditions have been established by trail and error. Good crystal boules are obtained using growth temperature 1050$^\circ$C for Vapour phase and 1300$^\circ$C
for melt growth techniques. Pulling rates of 0.4-0.6 mm/hr have yielded good crystal boules. Growth periods of 7-10 days are used. The grown crystals are found to be 0.6 cm dia and 1-2 cm in length. The growth rates are found to be smaller with increasing Cr concentration. The success rate in growth run is only 70%. The tip of the initial growth region of the growth tubes found to become brittle and was often found to break. This could be due to large strain developed in the initial growth region condensing several small grains resulting in large vapour pressures. Though there are some reports on Bridgman grown crystals of this system, no reports available on vapour phase growth in the literature.

5.2 CHEMICAL ANALYSIS

Chemical analysis carried out on the as-grown crystals by EDAX, showed that the estimated and target compositions are within ±0.03 at. %. This deviation might be due to incongruent vapourization and melting that might have resulted in leaving some charge unused (left over) and deposits on the walls of the growth tube.

5.3 SURFACE MORPHOLOGY

The morphological features revealed the existence of growth steps, propagating layers indicating inevitable participation of the dislocations associated with crystal anisotropy in a crystal growth. Thus it is concluded that the growth layers have the origin and propagation at and around screw dislocations.

5.4 STRUCTURAL ANALYSIS

X-ray diffraction studies revealed that the samples of all compositions with \( x = 0.001, 0.002, 0.003, 0.004 \) and \( 0.005 \) exhibited zinc blende structure. Single phase crystals of \( \text{Zn}_{1-x}\text{Cr}_x\text{Te} \) are obtained with \( x \leq 0.005 \). At higher concentrations of \( 'x' \) in addition to zincblende phase, phases of \( \text{CrTe} \) were also detected. The lattice
parameters for crystals of all compositions were found to increase linearly in the range 6.0968 - 6.1015 nm obeying Vegard’s law. As the concentration is increased, the grain size decreased from 483 to 375 nm and the crystallinity deteriorated.

5.5 MICROHARDNESS STUDIES

Microhardness studies on selected smooth surfaces of Zn$_{1-x}$Cr$_x$Te single crystals for $x = 0.001, 0.002, 0.003, 0.004$ and $0.005$ for different loads in the range of 0-200gm have been carried out using Vicker’s indentation method. The Vicker’s hardness ($H_v$) found to decrease exponentially with concentration ‘$x$’ for crystals of all compositions. Applications of more load (300-500 gm) resulted in breakage indicating the brittleness of the crystals.

5.6 REFLECTIVITY STUDIES

Reflectance spectra of pure ZnTe and Zn$_{1-x}$Cr$_x$Te with $x = 0.001, 0.002, 0.003, 0.004$ and $0.005$ in the wave length 200-2000 nm were recorded at room temperature. The values of band gaps and the corresponding transitions $E_0$ (2.26 eV), $E_0+\Delta_0$ (3.22 eV) $E_1$ (3.60 eV), $E_1+\Delta_1$ (4.15 eV) and $E_2$ (5.45 eV) in pure sample were found to be in agreement with the reported values of ZnTe. As the composition ‘$x$’ increased, the fundamental absorption edge ($E_0$) in Zn$_{1-x}$Cr$_x$Te shifted towards the higher energies (2.28 to 2.37 eV). Linear dependence of fundamental absorption edge ($E_0$) on composition ‘$x$’ is expressed by a straight line of the form $E_0(x) = 2.258 + 0.699x$.

A broad absorption band is observed in the diffuse reflectance spectra of all compositions around 5200 cm$^{-1}$ due to the transition of $^5T_2 \rightarrow ^5E$. This evidently shows that the Cr$^{2+}$ substitutionally enters into the divalent cation site (Zn$^{2+}$) of the host.
5.7 EPR STUDIES

Though the samples of all compositions are subjected to EPR characterization, samples with compositions $x = 0.001$ and 0.002 only responded showing paramagnetism at room temperature. The sample with composition $x = 0.001$ showed a broad resonance signal at $g = 1.9417$ overlapped with six hyperfine lines. A sharp resonance signal at $g = 1.9376$ with broad hump at $g = 2.4437$ is noticed for the sample with composition $x = 0.002$. The resonance signals in the spectra of the two samples are characteristic of $\text{Cr}^{2+}$ ion in tetrahedral symmetry. The hyperfine lines in spectra of the first sample and broad hump in the spectra of the second sample are due to $\text{Mn}^{2+}$. As the concentration is increased the resonance signal becomes sharper indicating a decrease in the number of spins.

5.8 MAGNETIC STUDIES

The samples of $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ with $x = 0.001, 0.002, 0.003, 0.004$ and 0.005 were characterized by VSM for magnetic studies. The samples with composition $x = 0.001$ and 0.002 exhibit a strong variation in magnetization with magnetic field with out any saturation. The shapes of the curves are independent of composition ($x$). This type of behaviour is obvious for low concentration of Cr in II-VI DMS which exhibit intermediate behaviour to Brillouin type of paramagnetism and Van Vleck type of paramagnetism.

As the composition ($x$) is increased beyond $x = 0.002$, the M-H measurements revealed the hysteresis behaviour exhibiting ferromagnetism at room temperature. The coercivity, saturated magnetism and area under hysteresis increased with composition ($x$). The observed ferromagnetism in the samples is attributed to intrinsic $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$.
5.9 RESISTIVITY STUDIES

Zn$_{1-x}$Cr$_x$Te crystals with composition $x = 0.001$, 0.002, 0.003, 0.004 and 0.005 are subjected to electrical resistance measurements in the temperature range 200-450 K. At room temperature the resistivities of all samples lie in the range 400 - 1500 $\Omega$cm. As the temperature is increased the resistivity is found to decrease with composition ($x$). This evidently shows the semiconducting behaviour of the samples. The hot probe test shows that the as-grown crystals have $p$-type conductivity.

CONCLUSIONS

- Zn$_{1-x}$Cr$_x$Te single crystals were grown successfully using Vapour phase and vertical Bridgman growth methods. Optimum growth parameters were obtained after a great deal of trial and error.

- The as-grown crystals were subjected to chemical analysis and the average composition was in agreement with 0.03 at. % of the starting compositions.

- The surface morphology studies of the samples revealed screw dislocations aided growth in the crystals.

- XRD studies revealed zinc blende structure of Zn$_{1-x}$Cr$_x$Te crystals. For concentrations $x > 0.005$ ($x=0.007$) in addition to zinc blende phase, phases of CrTe were detected. The lattice parameter varied linearly obeying Vegard's law.

- Microhardness studies on selected surfaces of Zn$_{1-x}$Cr$_x$Te crystals, revealed the plastic flow between the atomic chains of atoms with increasing composition ($x$).
Chapter V

Summary and conclusions

> Reflectivity studies showed a shift towards higher energies in the fundamental absorption edge \(E_0\) with composition \(x\). The reflectance spectra exhibited a broad band around 5200 cm\(^{-1}\), indicating that \(\text{Cr}^{2+}\) substitutionally enters the divalent cation site of the \((\text{Zn}^{2+})\) of the ZnTe host.

> EPR studies depicted paramagnetic state for \(\text{Zn}_{1-x}\text{Cr}_x\text{Te}\) samples with \(x = 0.001\) and 0.002.

> The magnetic studies on \(\text{Zn}_{1-x}\text{Cr}_x\text{Te}\) samples revealed that the samples with \(x = 0.001\) and 0.002 exhibited intermediate behaviour to Brillouin type of paramagnetism and Van Vleck type of paramagnetism. The samples with compositions \(x = 0.00, 0.004\) and 0.005 exhibited hysteresis behaviour at room temperature. The observed ferromagnetism is believed to be intrinsic to \(\text{Zn}_{1-x}\text{Cr}_x\text{Te}\).

> Electrical resistivity studies showed semiconducting behaviour of the samples in the temperature range 200-400 K.

FUTURE PLAN OF WORK

> The mechanism of ferromagnetism in \(\text{Zn}_{1-x}\text{Cr}_x\text{Te}\) system is still a subject of debate. To explore this, investigations on Magnetic Circular Dichroism (MCD), Hall Effect and Magneto-resistance studies down to low temperatures are essential.

> Investigation on dielectric properties and \(\varepsilon\) vs. \(\omega\) plots may give an insight into the relaxation mechanisms. This may help to understand the electrical transport mechanism in \(\text{Zn}_{1-x}\text{Cr}_x\text{Te}\) system.

The author therefore, is planning to take up the above mentioned investigations in future.