PREFACE

Nature is abundant in natural materials. Most of the naturally occurring compounds are inorganic and herbs as plants in nature in the Earth’s crust are solids. These are minerals, herbs, plants and trees etc. These compounds are widely used in medicine, chemical industries, agriculture and in daily life. Usage of bulk compounds in daily is very extensive. But use of quality compounds is very important.

Therefore a detailed study of a few mineral compounds containing transition metals have been carried out using XRD, electron paramagnetic resonance (EPR), Optical absorption and Near-infrared (NIR) studies. Different minerals are studied and their studies are presented in independent chapters. To understand basic theory involved in the study one more chapter is added along with literature review.

This thesis is spread into seven chapters.

Chapter - 1

In this chapter theoretical principles of XRD, EPR, Optical absorption and IR spectroscopy is described in brief.

Chapter - 2

Deal with the literature survey carried out on the studied minerals and synthetic samples. Literature review on the following was carried out using libraries in various institutes, journals and internet. The compounds are i) kyanite (Al₂O₃.SiO₂) mineral, ii) yellow ochre mineral, iii) manganese mineral ardennite, alleghanyite and leucopoenicite, iv) synthesized nano manganese oxalate (MnC₂O₄.2H₂O), and v) synthesized chloroapatite.

Chapter - 3

In this chapter the blue coloured kyanite(Al₂O₃.SiO₂) mineral obtained from Chitra Durga, Karnataka of India spectroscopic characterization studies were discussed. The mineral grading is dependent on percentage of Al₂O₃ content in it. Kyanite which contain above 60% of Al₂O₃ is called grade-1, if contain between 50-60% called grade -2 and less than 50% is called grade-3. Grade-1 contain maximum of Fe₂O₃ about 1.50 % including other impurities. Using X-ray diffraction (XRD) studies structure was
identified. The transitional metal ions were present in the structure was investigated using electron paramagnetic resonance (EPR) as well as optical absorption spectra. The EPR results were suggesting that Fe$^{3+}$ is entering in place of Al$^{3+}$ in the unit cell of kyanite. Optical absorption spectral studies were suggesting that Fe$^{3+}$ and Ti$^{3+}$ were present in the mineral. The impurities were playing the major role in the industrial application of the mineral which were identified upto ppm level using the above techniques.

Chapter - 4

In this chapter, yellow ochre mineral obtained from Vempalli mandal, Cuddapah district, Andhra Pradesh of India is investigated and its results are presented. The chemical analysis of yellow ochre indicate that Fe$_2$O$_3$ = 4.22 wt% and TiO$_2$ = 0.64 wt%. Structural characterization is performed using X-ray diffraction (XRD). XRD results suggest that goethite (Fe$_2$O$_3$) and quartz are present. Among them goethite is the major constituent. Its unit cell is orthorhombic with cell constants $a = 4.14$ Å, $b = 10.0$ Å, $c = 3.03$ Å. The ligands around the metal ion present in the structure are investigated using FTIR spectroscopy. Internal structure studied using TEM suggests that the mineral consists of needle shaped iron oxide nano particles and quartz formed as tetrahedral and octahedral layers. EPR results indicate that the unit cell of the crystal contains Fe(III), and its g values are found to be 4.19 and 2.13. FTIR properties are due to the presence of silicate and hydroxyl anions as ligands. Nonlinear optical measurements carried out using Z-scan reveal the presence of strong nonlinear optical limiting in the material, indicating potential applications in laser safety devices.

Chapter - 5

Putforths the study on manganese mineral ardenite, alleghanyite and leucopoenicite originated from Madhya Pradesh, India, Nagano prefecture Japan, Sussex Country and Parker Shaft Franklin Sussex Country, New Jersey. Alleghanyite $[\text{Mn}_5(\text{OH})_2(\text{SiO}_4)_2]$ is silicate mineral. Its color is pink to reddish brown. It belongs to humite group. Its cell constants are $a = 8.2747$ Å, $b = 4.8503$ Å, $c = 10.7193$ Å. Mn in the mineral is in distorted octahedron. Ligands around manganese are oxygen and hydroxyl. Ardennite $[\text{Mn}_4(\text{Al,Mg})_6(\text{Si}_5\text{O}_{18}) (\text{As,V})\text{O}_4(\text{OH})_6]$ is a rare arsenic manganous variety of gem silicate mineral. It belongs to orthorhombic group having cell constants $a = 8.712$ Å, $b = 18.512$ Å and $c = 5.8108$ Å. In this mineral MnO is about 20 wt% and iron is in traces.
Leucophenicite $[\text{Mn}_7\text{(SiO}_4\text{)}_4\text{(OH)}_2]$ is also a silicate mineral. It also belongs to the humite group of minerals. Its crystals are very rare. The mineral crystallizes in the monoclinic crystal system, space group 2/m with unit cell parameters $a = 10.84 \text{ Å}$, $b = 4.82 \text{ Å}$, $c = 11.32 \text{ Å}$, $\beta= 103.93^\circ$. This mineral contains about 60 wt% of MnO and FeO is in traces. EPR spectra of all the three minerals are similar. Also it reveal the presence of Mn(II) showing no hyperfine splitting with almost same $g = 2.0$ value and confirming that manganese is in very high concentration. Optical absorption spectrum of alleghanite and leucophenicite is due to Mn(II) and is in octahedral environment. In these minerals Fe(II) is noticed in traces. NIR results of all the three minerals are due to water fundamentals and confirming the formula of the minerals.

Chapter - 6(A)

Deals with the synthesized nano manganese oxalate ($\text{MnC}_2\text{O}_4\cdot\text{2H}_2\text{O}$). The natural manganese oxalate dihydrate $\text{MnC}_2\text{O}_4\cdot\text{2H}_2\text{O}$ is called lindbergite. It is a white to gray in color. This compound was synthesized by thermal double decomposition of oxalic acid dihydrate ($\text{C}_2\text{H}_2\text{O}_4\cdot\text{2H}_2\text{O}$) and $\text{Mn(OAc)}_2\cdot\text{4H}_2\text{O}$ solutions using a CATA -2R microwave reactor. The structure of the compound is carried out using X-ray diffraction (XRD). The unit cell constants obtained from the X ray spectrum is $a = 9.98 \text{ Å}$, $b = 5.40 \text{ Å}$ and $c = 12.45 \text{ Å}$. This result suggests that the compound adopts a distorted octahedral rhombic structure. Using XRD, X-ray density $d_x$ was calculated as $3.54\times10^3 \text{ kg/mm}^3$ and percentage porosity was 32. The particle size and shape were analyzed using transmission electron microscopy (TEM). These results suggesting that the particles were cylindrical and approximately 70 nm in size. The nano particles are very closely associated, which forms agglomerates. Over deposition of Mn in the compound indicates that formation of independent Mn oxalate nanorods. These are appears as a pattern that resembled palm tree leaves, a botanical plant species. The transition metal ion in the structure was investigated using electron paramagnetic resonance (EPR) as well as optical absorption spectra and near-infrared (NIR) spectroscopies.

EPR spectrum of the compound shows a single resonance line with $g = 2.130$, which is characteristic of Mn$^{2+}$ ion. This result suggesting that the majority of the nanocrystals contain more than one Mn$^{2+}$ ion. These results are in agreement with the TEM results. Furthermore, the Mn-based nanorods exhibited temperature-independent
paramagnetism. Optical absorption spectrum recorded in the range 200 – 1300 nm shows several energies. These spectral features are similar to Mn(II) when it is present in natural compounds. The nanocrystals produced with this method were pure and had a distorted rhombic octahedral structure. Using these energies crystal field splitting parameter $D_q$, and Racah parameters $B$ and $C$ are evaluated as $D_q = 900 \text{ cm}^{-1}$, $B = 600 \text{ cm}^{-1}$, $C = 2500 \text{ cm}^{-1}$ and $\alpha = 90 \text{ cm}^{-1}$. The NIR spectrum also recorded in the range 1300 -2500 nm. The observed bands in the spectrum are attributed to fundamental vibrations of water and the oxalates, which indicated that water molecules are not free but are bounded to the metal ions as ligands.

**Chapter - 6(B)**

Natural apatites are phosphate containing minerals. They are fluoro-apatite $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$, chloro-apatite $[\text{Ca}_5(\text{PO}_4)_3\text{Cl}]$, hydroxyapatite $[\text{Ca}_5(\text{PO}_4)_3\text{OH}]$, and carbonate-apatite $[\text{Ca}_3(\text{PO}_4,\text{CO}_3,\text{OH})_3(\text{F,OH})]$. It is the main constituent of teeth and bones. Also, it has wide application in the manufacture of fertilisers, phosphoric acid, fluorescent light. Copper doped chloro-apatite has been synthesized and characterized by XRD, TEM, Optical and NIR spectroscopy. Structural studies are characterized by XRD which indicates that the compound shows hexagonal structure with lattice constants of $a = b = 9.027 \text{ Å}$ and $c = 13.767 \text{ Å}$. The doping of cations like copper in the apatite lattice may leads to change the bulk properties. Therefore nano crystals of Cu doped chloro-apatite synthesized. Micro internal structure of the compound was studied using transmission electron microscopy (TEM). TEM images suggest that nano crystals are closely joined together and form agglomerates with rod in shape and are parallel. Optical absorption spectrum was characterized by the $\text{Cu}^{2+}$ in the Cu doped chloro-apatite, indicating that Cu(II) is in a tetragonal elongated distorted octahedral structure. Also copper is not entered in Ca two sites in equal proportions of the structure of the compound. The bands in NIR spectra are due to the overtones and combinations of water and phosphate molecules, which are supporting the formula of the compound.

**Chapter - 7**

Describes the results of investigations on core compounds. Further this chapter provides information on the scope of future work to be carried out on the studied compounds.