

PREFACE

For many centuries the word “crystal” was applied specifically to quartz, it is based on the Greek word implying a form similar to that of ice. In current usage, a crystalline solid is one in which the atomic arrangement is regularly repeated and which is likely to exhibit an external morphology of planes making characteristic angles with each other if the sample being studied happens to be a single crystal. When two single crystals of the same solid are compared, it will usually be found that the sizes of the characteristic plane “faces” are not in the same proportion the “habit” varies from crystal to crystal”. On the other hand, the interfacial angles are always the same for crystals of a given material.

The transition metal represents the filling of the atomic d-electron shell. Because the transition metals and their alloys typically have high melting temperature and hardness, their economic importance is immense. There has been rather little experimental work on phase transitions in transition metals because these elements are relatively incompressible yielding phase changes only at very high pressures beyond the experimental range.

Salen is the abbreviation for a popular chelating ligand used in coordination chemistry and homogeneous catalysis. The name salen is a contraction for salicylic aldehyde and ethylenediamine. The ligand is a bright yellow micaceous solid that is soluble in polar organic solvents. The diphenol H_2 salen is the conjugate acid of the ligand that logically is $salen^{2-}$. But the terminology is used loosely. As an anionic tetradentate ligand, $salen^{2-}$ resembles tetradentate ligands including those that are

macrocyclic, such as porphyrinate, corrin, bis(dimethylglyoximate), and some Schiff bases.

In 1938, T. Tsumaki reported that the cobalt(II) salen reversibly bound O_2 , and this finding led to intensive research on cobalt complexes salen and related ligands for the storage and transport of oxygen, i.e. synthetic oxygen carriers. SalenH₂ forms complexes with most transition metals. In many cases, the metal adopts square pyramidal or octahedral coordination sphere with the stoichiometry M(salen)L and M(salen)L₂. Illustrative examples include VO(salen) and Co(salen)Cl(pyridine). With d^8 metal ions, low-spin square planar complexes form, such as Ni(salen).

The work proposed in the thesis is divided into Eight Chapters.

Chapter 1 deals with the complete survey of the material used to developed crystals and the information regarding growth of this type of crystals. The current chapter deals with available and exciting information of ligand salen. This chapter also describes important of the transition metals and crystals growth from the combination of transition metal and ligands. The chapter also describe various basic crystal growth techniques and material identification for the manufacturing of crystal.

Chapter 2 describes the crystallization methods with their important parameter such as purification, perfection and different material growth technique with appropriate examples. The building unit and MoF(Metal-Organic Frameworks) also discussed in ongoing chapter. The complete crystal growth techniques are displayed in

current chapter. The synthesis of MoF completely describe in current chapter. In this chapter common ligand used in MoF are shown and discussed. Composite MoF materials and their synthesis are discussed in chapter. The salient features of Flux Method for Solid Crystal Growth used for the growth of crystals described. A detail of experimental set-up and required peripheral units used for crystal growth is also covered in this chapter. Flux and Reflux techniques with their required apparatus were complete explained in this chapter. Flux method is a method of crystal growth where the components of the desired substance are dissolved in a solvent (flux). The method is particularly suitable for crystals needing to be free from thermal strain and it takes place in a crucible made of non-reactive metal. A processing sequence, system type, heat flow, reaction which are very important parameter of the flux techniques were covered in this chapter. Heat source, condenser, heat control, heating bath, distillation, cooling bath which are very important part of reflux techniques were covered in this chapter.

Three methods to growth a crystals are also explained and their silent features described in current chapter. In current research work all three methods were used but crystal growth from method 3 - Rotary Evaporators are used for further research work by author. Specifications of spares required to particular techniques are covered in this chapter. This chapter also deals with preparation of material, preparation of schiffbase from ligand and preparation of crystal. Chemistry behind production of schiffbase and crystal growth with chemical formula is discussed in this chapter. Crystal of 1:1 Binary mixtures ($M^1 L_1$ or L_2 and $M^2 L_1$ or L_2) and 1:1:1 ternary mixtures ($M^1 L_1 L_2$ and $M^2 L_1 L_2$) were produced but crystals of ternary mixtures $M^1 L_1 L_2$ and $M^2 L_1 L_2$ were used for further work (where M^1 , M^2 are Co^{II} , Ni^{II} as required).

Chapter 3 deals with electrical and magnetic characterizations of the crystals. In current chapter theoretical aspect to measure electrical conductivity were discussed with their silent features and mathematical formulas. A low temperature resistivity and conductivity also describe in the current chapter with experimental aspect. High temperature resistivity also discussed with prior experimental setup but not studied further. To measure electrical conductivity of all crystal a crystal were combined and form a tablate of 6 mm diameter. Tabulate form of crystal was prepared by Rotary Tablate Machine which was discussed with their specification. High resistance electrometer was also discussed with their specifications in experimental unit.

Magnetic properties and types of magnetic behavior of crystals were discussed in ongoing chapter.

Chapter 4 deals with the optical characterizations such as Infrared absorption spectral study and Ultra Violet-Visible reflectance spectral study. The magnetic moment of the crystals are also derived and discussed in this chapter. The Molecular vibrations responsible for the optical spectra were covered briefly in ongoing chapter. The experimental setups for getting spectral characteristics (Infrared absorption and UV-Vis reflectance) are discussed in current chapter. The specification of Infrared spectrometer and UV-Vis spectrometer are displayed and discussed in current unit.

Infrared scanning for the schiffbase and crystals were made in the range $4000-600\text{cm}^{-1}$ in KBr. AR grade KBr was used for this purpose. It was first fused, powdered and dried in vacuum. The absence of moisture in this dried KBr pellet was checked by scanning the IR

spectra of purified KBr. Then the pellet of KBr with polymer was prepared as under.

A mixture of 4mg of pure dried sample and 1 gm KBr powder was ground in a mini ball mill for about 10 minutes. The resulting mixture was placed on the disc and compressed at high pressure about 20,000 psi giving the transparent pellet. The IR spectrum of this transparent pellet was scanned on Nicolet FTIR-760 spectrophotometer.

The anticipated IR spectral frequencies of all the samples are discussed in current chapter. The infrared spectra of crystals and schiffbase are also discussed in ongoing chapter. The inspection of the infrared spectra of all the samples are discussed.

In the present section, the results of the characterization of metal chelates(Crystals) by magnetic susceptibility measurement and reflectance spectral study are discussed in terms of structure-property relationship. This chapter also deals with the important aspect which are responsible to generates picks in UV Vis reflectance spectra such as metal to ligand charge transfer, ligand to metal charge transfer. In current chapter author completely discussed the result obtained from UV Vis reflectance spectra and responsible parameter crystal vise. On the basis of UV Vis spectral study and allowed transition the geometry of crystals were obtained and discussed.

According to geometry and optical study (IR and UV Vis spectra), the magnetic moment of all crystals were obtained and discussed briefly.

Chapter 5 covered thermal characterizations in the means of Thermogravimetric analysis and Thermal conductivity measurement. In current chapter different method for thermogravimetric analysis were discussed with their silent features. This chapter also explained the use of thermogravimetric analysis in different type of materials. The apparatus to obtained thermogram of the crystals were discussed. The factors affected to thermogram of the crystals were discussed briefly in the result and discussion. In present investigation, thermogravimetric analysis of the crystals was carried out in air by heating at a constant rate of 10°C per minute using a Perkin-Elmer TGA-7DSC-PYRIS-1-DTA-7 thermal analysis system. According the weight loss of the crystals as a function of temperature, the water molecular associate with crystals was explained in current chapter.

The thermal conductivity of the crystals was measured in ongoing chapter as a function of temperature. The theoretical background and sample and furnace preparation are also covered in this chapter. Common thermal conductivity measurement methods are briefly discussed with Material type, Temperature range in °C and Property range in W/(m.K). The Hot-Wire method was fully discussed in current chapter as author used this method for research work. An experimental apparatus with photograph and sample size were displayed in this chapter.

Chapter 6 deals with chemical study of the crystals. In current chapter elemental analysis and molecular conductivity of the crystals were obtained as a part of chemical analysis. An experimental setup of C-H-N-S-O elemental analyzer was discussed with their specification. An idea and fundamental background of Elemental analysis also discussed in this section of thesis.

Antibacterial Assay of Crystals was obtained as part of biological study of crystals in **Chapter 7**. The method and environmental nature of the crystal were discussed in current chapter.

Conclusions drawn from the entire work and scope for future work finds place in **Chapter 8**.