Chapter II

REAGENTS AND EXPERIMENTAL METHODS

The details regarding the ligands, metal salts and other reagents used are presented in this chapter. The experimental procedure and the methods adopted for the analysis of the crystals are also given.

2.1 Reagents

2.1.1 Ligands

The ligands used for the investigation are malonic acid (CDH), succinic acid (CDH), adipic acid (CDH) and fumaric acid (CDH). All the ligands used were of AR grade.

2.1.2 Metal salts and solvents

Methanol (Merk) and acetic acid (Merk) were of AR grade and used without further purification. Metal salts used were of AR grade and the solutions were prepared in distilled water.

2.1.3 Other reagents

Sodium metasilicate (CDH) used was of AR grade.

2.2 Experimental procedure: The silica gel technique

Gel diffusion technique is one of the easiest and low cost methods of growing crystals at room temperature. The various types of gels used in crystal growth experiments are silica gel (sodium metasilicate), agar gel (carbohydrate polymer), gelatin gel (resembles protein structure), clay gel, poly acrylamide, hydroxides in water, oleates, stearates etc. The silica gel made out of sodium metasilicate (SMS) is often used because of its easy availability and better
performance in growing many compounds. SMS is dissolved in distilled water and a solution with desired specific gravity (1.02-1.05 g cm\(^{-3}\)) is prepared. The specific gravity was measured using a hydrometer. The apparatus of the experiment consists of a single glass tube of length 20 cm and diameter 2.5 cm. 20 ml of sodium metasilicate solution is taken in the glass tube. The gel was prepared by adding ligand of particular molarity (0.125-1.5 M) drop by drop to the SMS solution with continuous stirring to avoid excessive local ion concentration, which may cause premature local gelling and make the final solution inhomogeneous. The solution with desired value of pH (3-7) was then transferred to several glass tubes. After setting the gel, an aqueous solution of metal salt (upper reactant) of desired molarity (0.125-1.5 M) is carefully poured along the walls of the tubes over the set gel. The gel medium provides a polymer grid permitting reactant to diffuse into the medium with a desirable control rate. The open ends of the test tubes are closed with transparent sheet of plastic to avoid evaporation of the solution and contamination of impurities.

2.3 Analysis of the crystals

2.3.1 Elemental analysis

Elemental analysis of carbon, hydrogen and nitrogen is the most essential investigation performed to characterize and prove the elemental composition of a sample. The carbon and hydrogen contents in the obtained crystals were determined by using Elementar Vario-EL 111 CHNS analyzer at Sophisticated Analytical Instrument Facility, Cochin University of Science and Technology (CUSAT), Kochi, India.

2.3.2 FT-IR spectral studies

FT-IR spectral studies measure the transmittance of infrared radiation by the sample material versus wave number. The infrared absorption bands identify molecular components and structures. The interpretation of infrared spectra involves the correlation of absorption bands in the spectrum of the unknown compound with the known absorption frequencies for types of bonds. FT-IR
spectra were recorded on potassium bromide pellets on a Thermo Nicolet Avatar 370 spectrometer in the range 4000-400 cm\(^{-1}\) at Sophisticated Analytical Instrument Facility, Cochin University of Science and Technology (CUSAT), Kochi, India.

2.3.3 FT-Raman spectral studies

Raman spectroscopy has become a very powerful tool for analysis and chemical monitoring because of its highly specific nature. FT-Raman spectra were recorded in the range 3500-50 cm\(^{-1}\) using a Bruker RFS 100/s spectrophotometer, operating at 1064 nm line of Nd:YAG laser as excitation wavelength with 150 mW power at Dental products Laboratory, Biomedical Technology Wing, Sree Chitra Tirunal Institute of Medical Science and Technology (SCTIMST), Thiruvananthapuram.

2.3.4 Powder X-ray diffraction studies

X-ray powder diffraction is a scientific technique for structural characterization of materials. Identification is performed by comparing the diffraction pattern to a known standard or to JCPDS file or to the Cambridge Structural Database (CSD). The powder X-ray diffraction studies were carried out using a Bruker AXS D8 advance XRD with Cu K\(\alpha\) radiation (\(\lambda = 1.54056\) Å). Goniometer radius is 217.5 mm. The detector used was solid state Si-Li detector. No monochromator was used and Ni was used as the filter. The analysis was carried out at Sophisticated Analytical Instrument Facility, Cochin University of Science and Technology (CUSAT), Kochi, India.

2.3.5 Single crystal X-ray diffraction studies

X-ray crystallography is a method of determining the arrangement of atoms within a crystal, in which a beam of X-rays strikes a crystal and causes the beam of light to spread into many specific directions. From the angles and intensities of these diffracted beams, a three-dimensional picture of the density of electrons within the crystal can be produced. From this electron density, the mean positions
of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other informations.

The crystallographic data were collected using Bruker AXS Kappa Apex2 CCD diffractometer, with graphite monochromated Mo Kα (λ=0.71073 Å) radiation at SAIF, CUSAT, Kochi and SAIF, IIT-Madras, Chennai, India. The program SAINT/XPREP was used for data reduction and APEX2/SAINT for cell refinement (Bruker, 2004). The structure was solved using SIR 92 (Altomare et al., 1993) and SHELXS-97 (Sheldrick, 1997) and refinement was carried out by full-matrix least square on $F^2$ using SHELXL-97 (Sheldrick, 2008). Molecular graphics employed were DIAMOND software Version 3.1 f (Brandenburg, 2008), MERCURY (Bruno et al., 2002) and X-SEED (Barbour, 2001).

2.3.6 Dielectric studies

The dielectric responses of the samples at room temperature were studied by H10K1 3532 LCR HITESTER in frequency range 300 Hz-3 MHz at National Institute for Interdisciplinary Science and Technology (NIIST), Thiruvananthapuram. The principle behind the measurement of dielectric constant is that of parallel plate capacitor. The powdered sample was shaped as pellets of diameter 11 mm and thickness 2 mm under the pressure of 100 Mpa. These pellets were then thinly coated with high purity air dry silver paste to make them into a parallel plate capacitor. Dielectric constant ($\varepsilon$) was calculated by the relation

$$\varepsilon_r = \frac{C \cdot \varepsilon_0}{A}$$

where $\varepsilon_0$ is the permittivity of the free space, $C$ is the capacitance, $t$ is the thickness of the sample and $A$ is the area of cross section.

2.3.7 UV-Visible spectral studies

UV-Visible spectroscopy involves the spectroscopy of photons in the UV-visible region. It uses light in the visible, adjacent near ultraviolet (UV) and near infrared (NIR) ranges. In this region of the electromagnetic spectrum, molecules
undergo electronic transitions. The absorption of UV or visible radiation corresponds to the excitation of outer electrons. The UV-Visible transmittance spectrum is recorded in the range 200-1200 nm in a Varian Cary 5000 UV-Visible-NIR spectrometer at SAIF, CUSAT, Kochi. The spectrum was used to determine the transmission range and the lower cut-off wavelength to know the suitability of the material for optical applications.

2.3.8 Thermogravimetry

Simultaneous TG-DTA measures both heat flow and weight changes in a material as a function of temperature or time in a controlled atmosphere. The technique can be used in the examination of thermal stability of a material together with the nature and processes involved in thermal decomposition and oxidation processes. The thermal studies of the grown crystals were studied using a Perkin Elmer Diamond TG/DTG analyzer instrument in nitrogen atmosphere. The analysis was carried out at SAIF, CUSAT, Kochi.

2.3.9 Microhardness studies

The mechanical behaviour of a crystal is very important in technological applications. The hardness of the material is identified as an important mechanical property. The hardness measurement is treated as an efficient technique of providing information about the elastic, plastic and viscous properties. Although hardness is one of the properties of which we are most conscious, it is very difficult to define it precisely so as to include all the various characteristics of a material which have been referred to as hardness. The precise definition depends entirely on the method of measurement, which will determine the scale of hardness obtained. Measurement of hardness is a useful nondestructive testing method to determine the bond strength. The microhardness value correlates with other mechanical properties like elastic constants. The hardness of a material depends on different parameters such as lattice energy, Debye temperature, heat of formation and interatomic spacing (Soni, et al., 2004; Chacko et al., 2006). During an indentation process, the external work applied by the indentor is converted into a
strain energy component which is proportional to the volume of the resultant impression and a surface energy component which is proportional to the area of the resultant impression (Dong et al., 2009). Microhardness studies of any system have direct correlation with the crystal structure and are very sensitive to the presence of other phases or phase transition present in the system. Microhardness indentations were made on the crystals using HMV-2T ADW microhardness tester fitted with a diamond pyramidal indenter and the indentation time was kept at 14 s. A diamond indenter is pressed into the surface of the crystal under the influence of a known load (10-100 g) and the size of the resulting indentation is measured. Hardness value is calculated from the expression $H_v = 1.854P/d^2$ kgmm$^{-2}$ where $P$ is the applied load in g and $d$ is the diagonal length in mm. The microhardness value was taken as the average of several impressions made. The analysis was carried out at Sree Chitra Tirunal Institute of Medical Science and Technology (SCTIMST), Thiruvananthapuram.

2.3.10 Nonlinear optical studies

The nonlinear optical conversion efficiency test was carried out using the Kurtz and Perry powder technique. It is a popular method to evaluate conversion efficiency of a nonlinear material. In this experiment, Q-switched pulses were obtained from a Q-switched Nd:YAG laser of wavelength 1064 nm. The crystals were ground to a particle size of 125-150 mm, packed in a micro capillary and then exposed to laser radiation with 10 ns pulse width. The output from the sample was monochromated to collect the intensity of 532 nm components and the fundamental was eliminated. The second harmonic radiation generated by the randomly oriented microcrystal was focused by a lens and detected by a photomultiplier tube. A strong bright green emission emerging from the mounted crystal shows that the sample exhibits good NLO property. KDP was used as a reference material for the present measurement. The nonlinear optical studies were carried out at IPC (Inorganic and Physical Chemistry), Indian Institute of Science (IISc), Bangalore.
2.3.11 Magnetic susceptibility

Magnetic susceptibility measurements were carried out in the polycrystalline state using Sherwood Scientific MK-1 magnetic susceptibility meter at Department of Chemistry, Govt. College for Women, Thiruvananthapuram. The effective magnetic moments were calculated from the equation

$$\mu_{\text{eff}} = 2.828 \sqrt{\chi_m} \times T \cdot B \cdot M$$

where $\chi_m =$ Molar magnetic susceptibility
$T =$ Temperature in Kelvin

2.3.12 Photoluminescence studies

Photoluminescence spectroscopy is a contactless, non-destructive method of probing the electronic structure of materials. Photoluminescence (PL) is the emission of light when a substance is irradiated with a shorter wavelength light. Quantum mechanically, photoexcitation causes electrons within the material to move into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released radiatively or nonradiatively. The radiative emission on photo-excitation is referred to as photoluminescence. The emission and excitation spectra of the samples are recorded using Fluoromax-3 spectrofluorometer consisting of 150W Xenon arc lamp, monochromator and a detector. The monochromatic excitation light is directed onto a sample, which emits luminescence. The luminescence is directed to a second emission monochromator which selects a band of wavelengths and shines them onto a photon counting detector (R928PPMT) ranging from 180-850 nm. The reference detector monitoring the Xenon lamp (a UV enhanced Si photodiode) requires no external bias and has good response from 190-980 nm. The signal from the detector is reported to a system controller and host computer where the data can be manipulated and presented using special software. Photoluminescence studies were carried out at the Department of Physics, Cochin University of Science and Technology (CUSAT), Kochi.