

2. LITERATURE REVIEW

This chapter deals with a brief review on various studies of nicotinic acid crystals, mandelic acid crystals, citrate crystals and phenylene diamine crystals.

2.1 STUDIES ON NICOTINIC ACID SINGLE CRYSTALS

(Clegg *et al.* 1995, Prasanna *et al.* 2011, Di *et al.* 2008 and Chen 2003) reported that pyridine derivatives possess a wide array of bioactivities and they are extensively used as ligands in the formation of co-ordination compounds. (Sheelarani and Shanthi 2015) mentioned that nicotinic acid, a B-vitamin, also known as niacin, and its associated complexes have a variety of pharmacological properties. Pyridine-3-carboxylic acid, generally known as nicotinic acid (NA), is a compound of considerable importance in terms of chemical, dietetic and therapeutic applications. Researchers have already analysed the synthesis, growth and characterization of certain nicotinic derivative, such as 4-aminobenzoic acid–nicotinic acid (Anandhi *et al.* 2011), nicotinium dihydrogenphosphate (Mythili *et al.* 2008), Nicotinium nitrate monohydrate (Dhanaraj *et al.* 2011), etc. Nicotinic L-Tartaric (NLT) crystal belongs to orthorhombic system with space group Abm2 and it belongs to soft material category. The TG/DT studies revealed that NLT single crystal is stable upto 212°C without any phase transition. SHG efficiency was observed as 66.6% of that of the standard KDP. So NLT crystals can be recommended for nonlinear optical applications.

(Anandhi *et al.* 2011) synthesised 4-aminobenzoic acid–nicotinic acid by dissolving 4-aminobenzoic acid and nicotinic acid in 2:1 ratio and using ethanol as solvent. The seed crystals were grown by slow cooling technique with spontaneous nucleation. The grown crystal 4-aminobenzoic acid–nicotinic acid was reported to have the monoclinic crystal system with the space group Cc. The unit cell lattice

parameters were identified as $a = 10.172 \text{ \AA}$, $b = 13.769 \text{ \AA}$, $c = 13.435 \text{ \AA}$ and $\beta = 99^\circ$. The functional groups were analyzed using FTIR Spectrophotometer in the entire region of $4000\text{--}400 \text{ cm}^{-1}$. The C=O stretch of COOH group gives its characteristic peak at 1663 cm^{-1} and splitting in this region is equal to nicotinic acid and 4-aminobenzoic acid carboxyl groupings. The thermogravimetric analysis revealed that there was a weight loss at about 150°C , which indicates the sublimable nature of the crystal.

(Lekshmi et al. 2015) reported that nicotinic acid (NA) is chemically pyridine-3-carboxylic acid. It is widely known as Niacin or Vitamin B3. The crystallisation of the cobalt complex of nicotinic acid was accomplished using gel diffusion technique. It was found that the asymmetric unit of cobalt nicotinate (CoN) consists of a nicotinic acid ligand, a cobalt ion and one co-ordinated water molecule. Considering the co-ordination environment in the CoN crystal, each cobalt ion is co-ordinated to two different nicotinic acid ligand through the pyridil nitrogen and to four water molecules. The four water molecules define an equatorial plane. The two nitrogen atoms of the nicotinate ligands occupy the axial position of the co-ordination sphere. The nicotinate ligand co-ordinate with Co ions monodentately. The nicotinate ligands are in trans position. From the FTIR spectrum of CoN it has been reported that the co-ordination of the metal with the organic linker is witnessed as the change in the molecular vibrational frequency. The TG/DT analysis of CoN revealed that the crystal is stable upto 160°C indicating the absence of lattice water. From the UV- Visible spectral studies the band gap of the material is obtained by extrapolating the linear portion of the curve to zero absorption and the value is estimated as 3.64 eV . (Wang *et al.* 2009) studied on the co-ordination complexes of nicotinic acid and its derivatives reveal their antiviral and antibacterial activity.

(Suksrichavalit *et al.* 2009) reported the synthesis of copper complexes of nicotinic acid with related pyridine derivatives. The copper complexes were shown to possess superoxide dismutase (SOD) and antimicrobial activities. (Wright and King 1950 and Kutoglu and Scheringer 1983) determined the crystal structure of nicotinic acid (NA) by growing it in 1:1 mixture of water and industrial spirit. Crystals were found to be twinned either about the *c* axis or across the 100 plane to a greater or lesser degree, and exhibited a fibrous structure. The optical properties were also studied. The reinvestigation was performed to derive more accurate parameters and to study the electron density distribution in the molecule.

(Arjun *et al.* 2017) synthesized 2-((2-ethylphenyl)amino)nicotinic acid (2EPNA) and its crystal structure was determined. It was observed that alkylation of the phenyl ring with ethyl group disrupts the planar conformation of the molecule by steric repulsion, resulting in formation of an acid-pyridine heterosynthon (instead of acid-acid homosynthon) in the crystal. Thermal properties of the compound were studied using differential scanning calorimetry (DSC). It is reported that the melting onset temperature of the crystal was at 135.6 °C with a heat of fusion of 80.8 J/g. The molten sample was then cooled at 20 °C/ min to -10 °C. During this cooling process the sample does not show any exothermic peak, indicating the formation of an amorphous solid. On re-heating at 10 °C/ min, the glass transition temperature (T_g) was observed at 38.4 °C. From the ¹³C SSNMR spectra it has been reported that 2EPNA has two alkyl carbon atoms, ¹³C and ¹⁴C, which are observed in the chemical shift range of 10–30 ppm for the crystalline and amorphous samples. (Deepa and Philominathan 2016) investigated how nicotinic acid as dopant in pure KDP (NAKDP) plays a vital role in enhancing the physical, chemical and mechanical properties of this novel NLO crystal. It has been reported that the SHG efficiency of

nicotinic acid-doped KDP crystal is 0.35 times greater than that of pure KDP. This is because of the delocalised π electrons in doped KDP which in turn enhance the polarisation effect under electric field component of the laser. It is also reported that both compounds NA and NAKDP show good inhibitory activities against all the bacteria strains, compared to standard drugs as positive controls used for comparison purposes. The antibacterial potent of the materials is due to synergistic effect, the nature of coordination of compounds, nuclearity of the compound, formation of chelate (Modiya and Patel 2012, Roy *et al.* 2014 and Liu *et al.* 2013).

(Sihui Long *et al.* 2016) discovered five crystal forms of 4-hydroxynicotinic acid (4-HNA), including three solvent-free polymorphs and two hydrates. Molecules that have been studied on tautomeric polymorphism include triclozadiazole (Tothadi *et al.* 2012), barbituric acid (Chierotti *et al.* 2008, Chierotti and Ferrero *et al.* 2010, Schimidt *et al.* 2011, Schimidt 2011), omeprazole (Bhatt 2007), ranitidine (Mirmehrabi *et al.* 2004), sulfasalazine (Blake *et al.* 2004), irbesarten (Bauer *et al.* 1998, Bocskei *et al.* 1998, Garcia *et al.* 2002), 2-amino-3- hydroxy-6- phenylazopyridine (Desiraju *et al.* 1983) and 2-(2,4-dinitrobenzyl)-3-methylpyridine (Schmidt 1999).

2.2 STUDIES ON MANDELIC ACID SINGLE CRYSTALS

(Omer Tamer *et al.* 2016) have reported that carboxylic acids are known as quite interesting building blocks for coordination compounds contributing to various roles through complexation such as one, two or more dentate coordination, bridging or chelating legends and counter-ions . Amid the organic system donor-acceptor charge transfer based hyperpolarizable compound possesses excellent third-order nonlinear optical properties compared to the more conventional inorganic compounds.

(Jayaprakash *et al.* 2016 and 2017) have reported that mandelic acid based single crystals are suitable for nonlinear optical applications. An organic conjugated chromophore DL-mandelic acid (DLMA) single crystal was grown by means of slow evaporation technique. Single crystal X-ray diffraction study proclaimed that the DLMA crystal crystallized in monoclinic system with centrosymmetric space group P21/c. The various characteristic fundamental vibration frequencies were identified by FTIR spectroscopic studies. UV-visible spectral analysis concluded that the lower cut-off wavelength and calculated direct optical band gap of DLMA as 257 nm and 5.40 eV respectively. Thermal property of DL-mandelic acid was established through thermogravimetric and differential scanning calorimetric technique. A careful examination of TGA profile, revealed that there is no weight loss up to 169°C which confirms the rejection of water molecules absorbed during the crystallization. TGA curve revealed that weight loss occurs in two steps and gradually decreases to zero weight. The DSC plot shows a sharp endothermic peak at 119°C endorsed the melting point of the DLMA.

(Jayaprakash *et al.* 2017) have also investigated and reported that the electric field response of DLMA crystal from the dielectric studies at a few selected temperatures 313K, 333K, 353K and 373K and frequencies from 50 Hz to 5 MHz. The total dipole moment (μ_0), mean polarizability (α_0) and first order hyperpolarizability (β_0) of DLMA is 1.1366 Debye, 1.5450×10^{-23} esu and 0.8190×10^{-30} esu respectively. The first order hyperpolarizability is 2.2 times greater than that of urea (β_0 of urea is 0.3728×10^{-30} esu). The results conclude that the DLMA molecule is a good candidate for NLO applications. In order to determine mechanical strength of DLMA crystal for various loads using Vicker's microhardness tester. The work hardening coefficient (n) value was found to be 4.17. The value of n suggests

that DLMA could be labeled as soft material. The real and imaginary parts of the third-order susceptibility (χ^3) were evaluated with the Z-scan technique using closed and open signatures respectively and was found to be $\text{Re}(\chi^3) = 4.15 \times 10^{-6}$ esu and $\text{Im}(\chi^3) = 0.47 \times 10^{-6}$ esu.

Wide range of investigations have been conducted to find out the stability difference between a pair of diastereomeric salts on the basis of crystal structures (Kinbara *et al.* 1996 and 2005, Kobayashi *et al.* 2005, 2006, 2007 and 2008, Suezawa *et al.* 2004, Yoshioka *et al.* 2000, Bialonska *et al.* 2006, Langkilde *et al.* 2002). (Quan He *et al.* 2010) reported that there is a growing interest in the pharmaceutical industry for the production of pure enantiomers of drugs, since a pair of enantiomers can have significant differences in pharmacological activity and determined the crystal structures of diastereomeric salts of chloromandelic acid and phenylethylamine. In general, there are three significant interactions in diastereomeric salt crystals; these are hydrogen-bonding, CH / π type interactions between aryl groups and finally Van der Waals interactions.

(Miao Yao *et al.* 2017) have synthesised four non-symmetric dimers containing mandelic acid as the chiral core. Chemical structures and liquid crystal (LC) properties of the dimers were characterised by FTIR, $^1\text{H-NMR}$, differential scanning calorimetry (DSC), thermogravimetric analysis (TG) and polarised optical microscopy (POM). The results indicated that the rigidity and conformation of the molecules of the dimers played important effects on their mesophase properties. LC dimers consist of molecules containing two mesogenic groups attached by a flexible spacer, which commonly are alkyl chains with an odd or even number of carbon atoms. Cholesteric liquid crystal (LC) have attracted great interest because the self-organisation of these structures can be controlled under external stimuli, including

temperature (Kosa *et al.* 2012, Tamaoki *et al.* 1999, Li 2013), pressure (Schmidtke *et al.* 2005), electric field (Hikmet *et al.* 1998, White *et al.* 2010), dopants (Kim and Tamaoki 2014, Kim *et al.* 2014, Delden *et al.* 2003, Tamaoki 2001, Tamaoki *et al.* 2000) and light (Li 2013, Kim and Tamaoki 2014). Cholesteric LC materials have been used in recent years because of their unique optical and electrical properties, which include selective reflection of light, thermochromism and potential applications such as optical-electro materials.

(Sivakumar *et al.* 2017) have developed single crystals of R-Mandelic Acid (RMA) by low temperature solvent evaporation method. These crystals were characterized using several techniques. Single crystal XRD analysis showed that RMA crystallizes in monoclinic crystal system and the measured cell parameters are $a = 8.666 \pm 0.019 \text{ \AA}$, $b = 5.870 \pm 0.006 \text{ \AA}$, $c = 15.206 \pm 0.020 \text{ \AA}$; $\alpha = \gamma = 90^\circ$, $\beta = 102.87^\circ$, and the cell volume $V = 754 \pm 2 \text{ \AA}^3$. As RMA was transparent from 267 nm to 1100 nm, it can be effectively used to convert the fundamental of Nd: YAG wavelength (1064 nm) into its second harmonic (532 nm). RMA can also be effectively used to generate other wavelengths employing other NLO processes. The TGA curve showed the thermal stability of the crystal was up to 201°C. Between 201°C and 310°C, the crystal completely decomposed. The endothermic peak obtained at 137°C may correspond to the RMA melting temperature. Successive endothermic peaks correspond to the decomposition of the crystal. The SHG efficiency of RMA was measured as 6.39 mJ. Third order technique n_2 , β and χ^3 were calculated using Z-scan analysis.

An amino acid based crystal exhibits high nonlinear optical efficiency because of its noncentrosymmetric space group and chiral carbon atom (Kitazawa *et al.* 1994, Misoguti *et al.* 1996). The efficiency can be increased by large delocalized π -electron

system with strong donor and acceptor groups (Zyss 1979, Levine *et al.* 1979). Amino acids contain a proton donor carboxyl acid (COO⁻) group and the proton acceptor amine group (NH₂⁺) with them. Molecular hyperpolarizability β is the basis for a strong second harmonic generation response. Organic crystals usually exhibit high β value and are good candidates for NLO applications (Patil *et al.* 2007).

(Sivakumar *et al.* 2018) have grown single crystals of R-Phenylalanine-S-Mandelic acid (RPSM) by slow evaporation solution growth method at 36°C. Single crystals of RPSM were grown by reacting R phenyl alanine (RPA) and S-mandelic acid (SMA) in 1:1 molar ratio by slow evaporation method. Transparent single crystals of RPSM were grown at the bottom of the beaker in a period of 30 days. The lattice parameters of the grown crystal were determined by X-ray diffraction analysis. It was determined that the grown crystal belongs to monoclinic crystal system and the measured cell parameters were $a = 19.88 \pm 0.03 \text{ \AA}$, $b = 5.56 \pm 0.009 \text{ \AA}$, $c = 17.10 \pm 0.03 \text{ \AA}$, $\alpha = \gamma = 90$, $\beta = 123.93 \pm 0.02^\circ$, and the cell volume $V = 1569 \pm 7 \text{ \AA}^3$. The vibrations of functional groups in the grown crystal were studied by Fourier transform infrared and Raman Spectral analysis. UV-Vis-NIR transmittance study was carried out to determine the cut-off wavelength and transmission range. The UV transparency cut-off wavelength of RPSM single crystal occurred at 351 nm. This suggests that the crystal can be used effectively in converting the Nd:YAG fundamental wavelength, 1064 nm, into its second harmonic, 532 nm and third harmonic, 355 nm. The thermal property of the grown crystal was investigated by TG/DTA analysis. The TGA curve showed that the crystal is stable up to 161°C. Then the crystal has undergone complete decomposition in several stages from 161°C to 610°C. Differential thermal analysis (DTA) curve showed endothermic peaks at 161°C, 198°C and 217°C. The first endothermic peak may correspond to the melting point of the crystal and the

successive peaks are due to the decomposition of the crystal. The molecular structure of the grown crystal was established by ^{13}C -NMR spectroscopy. Kurtz–Perry test was conducted for the powder form of grown crystal, which showed positive results for second harmonic generation (SHG). The SHG efficiency of RPSM was found to be 0.7 times that of KDP. Third order nonlinear optical properties were determined by Z-scan technique using He-Ne laser. Closed aperture Z-scan study reveals the positive nonlinearity in the crystal.

(Usha and Charles Kanakam Christopher 2016) have synthesized the organic non-linear optical compound bis-L-phenylalanine mandelate (BLPAMA) by the chemical reaction of commercially available DL- Mandelic acid and L-phenylalanine taken in the molar ratio 1:2 respectively by dissolving the mixture in water in a beaker, stirred well in a magnetic stirrer . The compound BLPAMA crystallized in monoclinic space group $P2_1$. The structure was resolved in noncentrosymmetric space group $P2_1$. The unit cell was indexed to a standard setting of $a = 5.4369 \text{ \AA}$, $b = 16.278 \text{ \AA}$, $c = 14.2654 \text{ \AA}$ and $V = 1257.5 \text{ \AA}^3$. The ^1H NMR and ^{13}C NMR studies confirmed the structure of the compound. Functional groups in the compound were identified using FTIR spectrum. The cut-off wavelength of BLPAMA crystal was found to be 240 nm. The absence of absorption in the entire visible region indicates the crystal has suitable opto electronic applications. The TGA thermogram showed a three stage decomposition and an inflection point at 190° C corresponds to the onset of material decomposition. The melting point of the material was 184°C , confirmed the thermal stability of the crystal and supports the utility for NLO applications. SHG efficiency of the compound BLPAMA was 56% with that of KDP.

2.3 STUDIES ON CITRATE SINGLE CRYSTALS

The available reports on citrates are Gallium Citrate, Iron (II) Citrate, Magnesium Citrate decahydrate, Manganese Citrate, Potassium Dihydrogen Citrate, Sodium and Lithium Dihydrogen Citrates, Triammonium Citrate, Trisodium Citrate, Zinc Citrate etc., (Paul O'Brien *et al.* 1997, Tadeja Birsa Celic *et al.* 2013, Prashant Dwivedi *et al.* 2010, Matzapetakis *et al.* 2000, Zeynep Yarbas *et al.* 2011, Jenny Pickworth Glusker *et al.* 1965). (Venkateshwarlu *et al.* 1989) has reported the growth and characterization of Triammonium Citrate. Tri Sodium Citrate Pentahydrate crystal structure was reported by (Burns *et al.* 1954). Nucleation studies were reported by (Junyan Gao *et al.* 2012). (Suneetha and Rajan Babu 2018) reported that semi organic or metal organic crystals possess good qualities from both organic and inorganic. Trisodium Citrate Pentahydrate (TSCP) single crystal was grown and their properties were reported by (Suneetha and Rajan Babu 2018). The crystal system was identified as orthorhombic with space group P_{nma} . The material shows low absorption in ultraviolet region and there is no absorption in the entire visible region. It has good transmittance of 64.9 % with lower cutoff wavelength at 235.9 nm. The low absorption in the entire UV and visible region is a potential requirement for NLO application. Vicker's micro hardness analysis says that the crystal has good mechanical stability and also belongs to the hard materials category. The low value of dielectric constant and dielectric loss at higher frequencies showed that the suitability of TSCP for NLO applications.

Citrate crystals find application in wide variety of fields. The use of citrate and tartrate salts as additives in copper plating baths to improve the quality of electrodeposited copper has been widely reported (Jiaqi Ni *et al.* 2017).

Citrate and Phosphocitrate (PC) are both recognized to be strong inhibitors of

the nucleation, growth and aggregation of Calcium Oxalate Monohydrate (COM) crystals (Richardson *et al.* 1990, Sallis *et al.* 1991 and Tiselius *et al.* 1993). (Wierzbicki *et al.* 1994) studied binding of citrate and phosphocitrate to calcium oxalate monohydrate crystals using scanning electron microscopy and molecular modeling. Phosphocitrate structure has been resolved using low temperature X-ray analysis and *ab initio* computational methods.

(Roger Qiu *et al.* 2004) reported that citrate strongly influences the growth morphology and kinetics on the (-101) face but has much lower effect on the (010) face. Moreover, binding energy calculations showed that the strength of the citrate-COM(calcium oxalate monohydrate) interaction is much greater at steps than on terraces and is highly step-specific. (Bravais 1866, Donnay 1937, and Friedel 1907) suggests that a platy morphology for dirubidium hydrogen citrate, with {020} as the principal faces might be expect.

(Peramaiyan *et al.* 2014) have grown Ammonium p-toluenesulfonate single crystals (AMPTS). The unit cell parameters, the morphology of AMPTS crystal were found out by single crystal X-ray diffraction study. The calculated cell parameters were $a = 20.411 \text{ \AA}$, $b = 7.066 \text{ \AA}$, $c = 6.272 \text{ \AA}$, volume $V = 904.6 \text{ \AA}^3$ and $Z = 4$. The grown crystal belongs to orthorhombic crystal system with noncentrosymmetric space group $Pna2_1$. It was also reported that ammonia is a weak base that gains a proton in acidic solution and forms the salt of the respective acid. During the proton transfer reaction, a proton is transferred from the electron donor group of p-toluenesulfonic acid to the electron acceptor group of ammonia. From the molecular structure of ammonium p-toluenesulfonate, it is inferred that the main fragment of the crystal to provide enhanced second harmonic generation efficiency may be due to the relatively delocalized electronic cloud of the sulfonate group of p-toluenesulfonate moiety. The

TG curve showed three stage weight loss pattern when the material was heated from 29 to 450°C. The first weight loss was occurred between 300 and 340°C with the elimination of 2.5 % of the material into gaseous products. The second stage weight loss noticed between 325 and 351°C experiences a weight loss of about 6.2 %. The third stage decomposition occurred between 353 and 385°C incurs a weight loss of about 78 %. An endotherm appeared at 145°C is assigned to the melting point of AMPTS crystal. The endotherms appeared at 327, 348 and 365°C are matched with the successive weight losses in TG curve. Thus, the AMPTS crystal could be exploited for any applications below 145°C. From the dielectric study, it was concluded that the AMPTS crystal exhibits normal dielectric behavior.

The crystal structure of citrate salt was studied by (Love and Patterson 1960) and of double citrate salt by (Zacharias and Glysker 1993). The solubility study was explained by (Thomas and Van Auken 1991). (Pandya *et al.* 2017) carried out the growth of Potassium dihydrogen citrate (KDC) crystals and studied its characteristics. The crystal structure of KDC showed triclinic symmetry with lattice parameters $a = 11.820 \text{ \AA}$, $b = 14.970 \text{ \AA}$, $c = 9.442 \text{ \AA}$ with angles $\alpha = 91.60^\circ$, $\beta = 93.35^\circ$ and $\gamma = 110^\circ$. Thermo-gram of KDC crystals shows that the crystal is stable up to nearly 95°C. (Aygun 2013) performed structural study by (atomic force microscope) AFM & (scanning electron microscope) SEM of (vanadyl ion) VO^{+2} doped KDC with different magnifications and also carried out (electron paramagnetic resonance) EPR study of (copper ion) Cu^{+2} and VO^{+2} doped KDC. (Zeynep Yarbasi *et.al.* 2011) done EPR and optical study of vanadium doped KDC.

The citrate structure has been characterized previously by X-ray analysis (Glusker 1980). (Mashkovskiy and Lekarstvennye Sredstva 2008, Briand and Burford 1999, Yukhin Yu) reported that Bismuth compounds are used in medicine for more

than two centuries as astringent, abducing and anti-acid agents, and as the means to treat infections. Drugs based on bismuthpotassium citrate are winning wide application during the recent years to treat the diseases of gastrointestinal tract. It was demonstrated (Hermann, Herdweck and Pajdla 1991) that the compound with the composition $\text{KBiC}_6\text{H}_4\text{O}_7 \cdot 3\text{H}_2\text{O}$ gets crystallized at 8°C from the aqueous solution of bismuth tripotassium dicitrate which is used to treat gastrointestinal tract. The interaction of bismuth nitrate with potassium citrate in water-glycerol (33.3 vol.%) solutions was studied (Palkina *et al.* 2005 and Antsyshkina *et al.* 2006). (Naidenko *et al.* 2012) prepared the compound $\text{KBiC}_6\text{H}_4\text{O}_7 \cdot \text{H}_2\text{O}$ by using the products citrate ions/bismuth/potassium/water in the molar ratio 1 : 1 : 1 : 1. From the IR spectrum of bismuth-potassium citrate it was observed the disappearance of the characteristic bands of carbonyl absorption (1745 , 1708 and 1429cm^{-1}). Instead, the bands of stretching symmetric and asymmetric vibrations of COO^- groups appear (1607 and 1439 , 1379cm^{-1}), which is the evidence of deprotonation of the carboxylic groups of citric acid (Bellamy L 1958). Decomposition of citrate ions in the oxidative atmosphere starts at about 220°C .

(Alagappa Rammohan and James 2017) have solved the crystal structure of dirubidium hydrogen citrate, $2\text{Rb}^+ \cdot \text{HC}_6\text{H}_5\text{O}_7^{2-}$. The crystal system was found to be monoclinic with space group $\text{P}2_1/\text{m}$ and the lattice parameters $a = 5.97796\text{ \AA}$, $b = 15.0960\text{ \AA}$, $c = 5.32067\text{ \AA}$ with angles, $\beta = 93.9341^\circ$.

(Kampf and Mills 2010) used the crystal-structure analysis to identify crystals of $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$ on a specimen of hematite pseudomorphous after magnetite from the Payu 'n Matru' volcanic field, Mendoza Province, Argentina. The compound was identified as triclinic, with $a = 6.3434\text{ \AA}$, $b = 6.4566\text{ \AA}$, $c = 12.0640\text{ \AA}$, $\alpha = 99.233(7)$, $\beta = 102.810(7)$, $\gamma = 101.562(7)^\circ$ and $Z = 2$. The crystal structure,

consists of a zig-zag chain of 9-coordinated Pb^{2+} atoms along **b**. Chains were linked together by citrate molecules to form thick irregular layers in the *ab* plane. The layers are linked together only by H bonds. The citrate molecule exhibits normal bond lengths and angles. The Pb^{2+} atom exhibits markedly lopsided coordination due to the $6s^2$ lone-electron-pair effect. The lone electron pairs on alternating sets of adjacent Pb^{2+} atoms in the chain point towards one another. The formation of the $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7)\cdot\text{H}_2\text{O}$ crystals was the result of specimen cleaning in citric acid. The cleaning solution was apparently contaminated through the dissolution of minor associated Pb bearing species by the citric acid.

2.4 STUDIES ON PHENYLENE DIAMINE CRYSTALS

(Motoharu Tanaka and Takuji Kawasbma 1964) reported that o-Phenylenediamine and its derivatives, 4- nitro-o-phenylenediamine , 4-chloro-o-phenylenediamine and 4methyl-o-phenylenediamine reacted with selenous acid in acid solution and formed benzoselenadiazoles, that can be formed into toluene. The molar extinction coefficient, optimum conditions of formation, distribution ratio and wavelength of maximum extinction were studied for each benzoselenadiazole. There is an interference of Iron(III) and molybdenum(VI) due to the determination of selenium with these reagents, and the interference was overcome by ethylenediaminetetraacetic acid (EDTA) in the above cases. Vanadium (V) interference was there only in 4-chloro- and 4-nitro-o-phenylene- diamines, and EDTA cannot remove this interference. It was concluded that O-Phenylenediamine and 4-methyl-o-phenylenediamine can be observed as good selective reagents to determine selenium when used along with ethylenediaminetetraacetic acid (EDTA). 4-methyl-o-phenylenediamine is better because of the high distribution ratio of 5-methyl- benzoselenadiazole. When iron (III), vanadium (V), tin (IV) and chromium

(III) are separated by extraction as from an acidic medium, the other reagents, and 4-chloro-o-phenylenediamine, could be used successfully. So these two o-diamines, especially 4-nitro-o-phenylenediamine can be used to determine selenium in strongly acidic solution.

The organic eutectics and intermolecular compound (IMC) are the organic analogs of metallic eutectics and inter-metallic compounds and these systems open the opportunities to unravel the mysteries of various aspects of crystallization at low temperature. (Rai, Manjeet Singh and Rai 2017) prepared the IMC using the green synthesis by solid state reaction between 2-hydroxy-1, 2-diphenylethanone (HDPE) and 4-nitro-o-phenylenediamine (NOPDA) in 1:1 M ratio. By slow evaporation technique single crystal of the IMC was grown from saturated solution of the materials HDPE and NOPDA in acetone at room temperature. The resultant complex was purified by crystallization using analytical grade ethyl acetate solvent. From the single crystal X-ray diffraction analysis it was found that the IMS crystallizes in monoclinic unit cell with C2/c space group. The dielectric constant and loss values of the IMC at room temperature were found to be in between those of the parent compounds NOPDA and HDPE. It was observed that the dielectric constant and loss values of IMC decrease exponentially with increasing frequency, and those of the parent components and binary compound are almost constant except at lower frequency (below 1 kHz).

(Leela *et al.* 2014) synthesized 4-chloro-4-methoxy-benzylideneaniline (CMOBA) by slow evaporation method. It was found that the grown crystal belongs to orthorhombic crystal system and the measured cell parameters were $a = 6.102 \text{ \AA}$, $b = 7.357 \text{ \AA}$, $c = 27.555 \text{ \AA}$, and the cell volume $V = 27.469 \text{ \AA}^3$. The lower cutoff wavelength of CMOBA was found to be at 390 nm and a wider range of transparency

was observed. Second harmonic generation (SHG) test confirmed the green emission with wavelength 532 nm. The SHG efficiency was found to be 3.7 times that of KDP. From the single beam Z-scan studies the two-photon absorption coefficient was measured as 3×10^{-12} m/W. Thermal analysis indicates that the grown crystal is stable upto 125°C.

Synthesis of 4,5-Diethyl-o-phenylenediamine through the Nitration of o-diethylbenzene was done by (John P Lambooy, 1949). The melting point was found to be 114-115°C and it was found to sublimes at 78° at 2mm mercury pressure. In addition to this several new compounds like 1,2-Diethyl-4-nitrobenzene , 3,4-Diethylaniline , 4,5-Diethyl-2-nitrocarbethoxyanilide, 4,5-Diethyl-2-nitroanili were involved as intermediate compounds during the preparation of 4,5-Diethyl-o-phenylenediami.

On the basis of the above literature survey, the materials 6methyl nicotinic acid (6MNA), ammonium citrate dibase (ACD), acetyl mandelic acid (AMA) and diammino nitro benzene (DANB) were chosen for current investigation. It was inferred from the review that materials of these families were proved to have SHG efficiency and could be used in laser technology, optical communications, optical data storage devices and high-speed information processing.