CHAPTER - 2

LITERATURE SURVEY

2.1 INTRODUCTION

In recent years, organic non-linear optical (NLO) crystals have gained considerable attention due to their relatively high nonlinearity and fast response. Particularly, third order nonlinear optical (TONLO) organic materials have gained much consideration because of their promising applications in optical switching, optical data processing, optical limiting, signal processing and ultrafast optical communications, etc. Today, crystal growth technology has advanced rapidly for the development of novel nonlinear optical materials (NLO) for various applications such as optical switching, frequency conversion and electro-optical modulation. Organic crystals have compounds with carbon atoms as their essential structural elements. The design and synthesis of organic molecules exhibiting NLO properties have been motivated by the tremendous potential for their applications in the fast developing domains of optoelectronics and photonic technologies. Organic materials attract much interest to chemists, material scientists and optical physicist because of their superior performance with respect to NLO properties such as the large NLO efficient, ultrafast nonlinear response time, and high optical damage threshold. The inorganic NLO materials have excellent mechanical and thermal properties but possess relatively modest optical nonlinearities due to lack of extended π-electron delocalization. In particular, the inorganic derivatives of protein amino

acids are often attributed to symmetric groups without an inversion Centre mostly to polar symmetry groups. Their crystals have properties whose symmetry is described by odd rank tensors such as pyro-electric effect, spontaneous electric polarization, piezoelectric effect, generation of second optical harmonics, etc. Semi organic crystals have large damage threshold, wide transparency range, less deliquescence, excellent nonlinear optical coefficient, low angular sensitivity and exceptional mechanical properties. The role of characterizing the crystal gain significance in the context that the results of such studies will give a feedback about the quality of the grown crystals so that the growth parameters will be standardized.

2.2 SLOW EVAPORATION SOLVENT TECHNIQUES

Saravanan et al. (2014) have presented single crystals of Lithium Hydrogen phthalate dihydrate (LHP), a semi-organic nonlinear optical material have been successfully grown from aqueous solution, by slow evaporation solution growth technique. Single crystals in size 40 X 10 X 5 mm^3 were grown in a period of 2 weeks. The grown crystals were characterized by single crystal X-ray diffraction. LHP crystallizes in Pnm space group of Orthorhombic system, with the unit cell dimensions at 293 K; a = 16.8356 Å; b = 6.8187 Å; c = 8.1967 Å; $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$. Third order non-liner studies have also been studied by Z-scan techniques. Nonlinear absorption and nonlinear refractive index were found out and the third order bulk susceptibility of compound was also estimated.

Effect of L-threonine (LT) doping on crystalline perfection, second harmonic generation (SHG) efficiency, optical transparency and laser damage threshold (LDT) in potassium di-hydrogen phosphate (KDP) crystals grown by slow evaporation solution technique (SEST) has been investigated by **S. K. Kushwaha et al. (2010)**. The influence of doping on growth rate and morphology of the grown crystals has also been studied. Powder X-ray diffraction data confirms the crystal structure of KDP and shows a systematic variation in intensity of diffraction peaks in correlation with morphology due to varying LT concentration. No extra phase formation was observed which is further confirmed by Fourier Transform (FT) Raman studies. High-resolution X-ray diffraction curves indicate that crystalline perfection has been improved to a great extent at low concentrations with a maximum perfection at 1 molar % doping. At higher concentrations (5 to 10 molar %), it was slightly reduced due to excess incorporation of dopants at the interstitial sites of the crystalline matrix. LDT has been increased considerably with increase in doping concentration, whereas SHG efficiency was found to be maximum at 1 molar % in correlation with crystalline.

Khanum and Podder (2011) they presented triglycine sulfate crystal and potassium bromide doped triglycine sulfate crystals were grown from aqueous solution by slow evaporation method. Energy dispersive X-ray analysis identifies the elements present in the crystal. The Fourier Transform Infrared spectroscopy has been recorded in the range 400 to 4000 cm^{-1} and the functional groups of the grown crystals have been identified. The structural

studies on the grown crystals were carried out by X-ray diffraction analysis technique and found that the grown crystal crystallizes in monoclinic structure. The lattice cell parameters of pure Triglycine sulfate are a = 9.6010 Å, b = 12.5600 Å, c = 5.4500 Å. Ultraviolet-Visible spectra show that the grown crystals have wide optical transparency in the entire visible region.

Samuel et al. (2013) they presented Single crystals of pure and L-glutamic acid doped Zinctris (thiourea) Sulphate (ZTS) were grown from aqueous solution by slow evaporation technique. The grown crystals were subjected to various studies such as FTIR, Powder X-ray diffraction, second harmonic generation (SHG), UV visible spectra and thermal analysis (TG-DTA). The FTIR study confirms the incorporation of L- Glutamic acid into ZTS crystal. The enhancement of SHG efficiency was observed in doped ZTS crystal. The doped crystals are optically transparent and thermally stable.

Prasanyaa et al. (2013) they have grown optically transparent Cu^{2+} and Cd^{2+} doped l-Arginine TriFluoroacetate (LATF) single crystals were grown from its aqueous solution using the slow solvent evaporation technique. The grown crystals were characterized by powder X-ray diffraction to confirm the monoclinic crystal structure. The percentage of transmittance measured using the ultraviolet–visible–near infrared spectrophotometer was found to be more than 80% for doped crystals. The functional group analysis of the grown crystals has been made by Fourier transform infrared spectroscopy. Thermo gravimetric/differential thermal analysis was performed for the grown crystals. An atomic absorption study was carried out to determine the presence of

Cu^{2+} and Cd^{2+}. The hardness of the grown crystals was assessed and the results show a significant variation in the hardness value between the pure and doped LATF crystals.

Prasad et al. (2015) they presented europium doped L-Tartaric acid; a non-linear optical single crystal was grown by slow evaporation solution growth method. The grown crystal was characterized by XRD for phase analysis, HRXRD for crystalline perfection, functional group by FTIR spectroscopy and powder SHG measurement for getting an estimate of NLO efficiency. The emission spectrum of Eu^{3+} doped L-Tartaric acid obtained after excitation at 394 nm and corresponding excitation spectrum by monitoring at 615 nm emissions. The decay curve is recorded corresponding to the $5D_0$ level of Eu^{3+} from tartaric acid doped with europium ions.

Amuthambigai and Shajan (2014) Potassium hydrogen phthalate (KHP) is a semi-organic crystal. Pure and amino acids like L-Histidine and L-Aspartic acid doped single crystals were grown from aqueous solution by slow evaporation technique at ambient temperature. The grown crystals were characterized by FT-IR, UV-Vis spectral studies and powder X-ray diffraction studies. The material of the grown crystals was confirmed by powder X-ray diffraction studies. The powder X-ray diffraction data compares very well with the JCPDS data. The lattice parameters and volume of the pure and doped crystals were calculated. Functional groups and modes of vibrations were identified from FT-IR bands. Optical transmittance was determined for the pure

and doped KHP crystals. It reveals that the grown crystal possesses very low absorption in the entire visible and IR region for both pure and doped crystals.

Shejwal et al. (2014) they presented a glycine doped bis-thiourea cadmium format (BTCF) crystal has been grown by a slow solution evaporation technique. The shifts in vibrational frequencies of different functional groups of BTCF were identified by Fourier transform infrared (FT-IR) spectral analysis. UV-visible studies were employed to assess the optical transparency of pure and doped BTCF crystals. The optical band gap of doped BTCF is found to be 5.16 eV. The optical constants, refractive index, reflectance, and optical conductivity have been evaluated, using the transmission data. The dielectric characteristics of pure and doped BTCF were investigated by employing dielectric studies. The decomposition temperature of pure and doped BTCF crystals was determined by using thermo gravimetric analysis.

Thilagavathy et al. (2014) they presented the single crystals of Potassium Hydrogen Phthalate doped with amino acid L-Lysine were grown successfully by slow evaporation method. The concentration of dopant in the mother solution was 0.5 molar %, 1 molar % and 2 molar %. There was a drastic change in the morphology due to variation in doping rates which is also reflected in the X-ray diffraction data. The Fourier Transform infrared spectroscopy study confirms the incorporation of L-Lysine into Potassium Hydrogen Phthalate crystal. The thermal study indicates the dissociating nature

of the crystal. The nonlinear optical property of the grown crystal has been confirmed by Kurtz powder second harmonic generation test.

Lakshmi and Mohan (2016) they presented the single crystals of L-Alanine doped with Potassium Chloride semi-organic crystals were grown by a Slow evaporation method in the ratio 1: 0.25, 1: 0.5, 1: 0.75 , and 1:1. The identities of the crystals were confirmed by Single crystal X-ray diffraction studies, Powder crystal diffraction studies. The modes of vibration of different molecular groups present in L-Alanine Potassium chloride were studied by FTIR and UV-Vis spectral analysis. Its NLO efficiency is estimated by Kurtz and Perry powder technique.

Kannan et al. (2013) they presented the Lanthanum doped Sulphamic Acid (SA) single crystal was grown by slow evaporation solution growth technique. The Presence of Lanthanum was confirmed by EDAX. The unit cell parameters of the grown crystal were confirmed by single crystal X-ray diffraction. The functional groups of the grown crystal were found by FT-IR study. Thermal and UV-vis absorption studies were performed to know the thermal and optical behaviors of the grown crystal respectively.

Chandra et al. (2013) they focus mainly on growing good quality crystal from amino acids and amino acid-based materials for nonlinear optics (NLO) applications. For the first time, a series of amino acid complexes doped with transition metal ions were grown inour laboratory from aqueous solutions by slow evaporation technique. Ni(II) ion doped Manganese

L-Histidine hydrochloride monohydrate (Ni(II)-MnLHICl) crystals were grown on the same lines and were characterized by powder X-ray diffraction (XRD), optical absorption, electron paramagnetic resonance, and infrared absorption studies.

Undoped and amino acid doped good quality single crystals of Sodium Acid Phthalate crystals (SAP) were grown by slow evaporation solution growth technique which are semi organic in nature. The effect of amino acid (L-Valine) dopant on the growth and the properties of SAP single crystal were investigated by **Nirmala and Prakash (2013)**. The single crystal X-ray diffraction studies and FT-IR studies were carried out to identify the crystal structure and the presence of functional groups in undoped and L-Valine doped SAP crystals. The transparent nature of the grown crystal was observed using UV–Visible spectrum. The thermal decomposition of the doped SAP crystals was investigated by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA).

Goel et al. (2013) they presented the pure and Zinc doped sodium phthalate (SP and ZSP) non-linear optical crystals have been grown by slow evaporation solution technique (SEST) at room temperature. Doped crystals exhibit prominent morphological changes (hexagon to pentagon) in different crystallographic planes. XRD revealed that metallic dopant (Zn) did not change the basic structure of the parent crystal. The presence of various functional groups and chemical bonding present in the crystals was identified and assigned qualitatively by Fourier transform infrared (FTIR) and Raman

analysis. UV–Vis studies indicate the low percentage of absorption in doped crystals in the visible region, thereby confirming the enhancement of non-linear optical (NLO) property. Second harmonic generation efficiency also gets enhanced as a result of metal ion Zinc doping. Dielectric analysis reveals that on Zinc doping dielectric constant and loss decreases significantly. In thermal analysis, the melting point and thermal stability of the SP crystals has been found to increase as a result of Zn doping.

Viruthagiri et al. (2013) they presented single crystals of pure and L-Histidine doped Thiourea (LHTU), an organic nonlinear optical (NLO) material; have been grown by slow evaporation technique at room temperature. The crystalline nature of grown crystal was confirmed by powder X-ray diffraction analysis (XRD). The functional group of the grown crystals was found by FTIR analysis. The spectral bands have been compared with similar Thiourea complexes using FTIR spectrum in the range 400 to 4000 cm^{-1}. The UV-Vis study was performed to know the optical behavior of the grown crystals. Surface morphology was studied by scanning electron microscopy (SEM) analysis.

Prasanyaa et al. (2014) they presented optically transparent L-arginine trifluoroacetate (LATF) single crystals by doping with organic materials urea and thiourea were grown by slow solvent evaporation technique. Powder X-ray diffraction confirms improvement in the crystalline quality for urea doped crystals. Urea doping in LATF also improves the percentage of transmittance. The vibrational frequencies of the grown crystals were assigned by Fourier

Transform infrared spectroscopy. The thermal analysis (TG/DTA) indicated the better thermal stability for urea doped LATF crystals. EDAX analysis was carried out to calculate the percentage of elements present in doped and pure LATF. The hardness has been remarkably improved on urea and thiourea doped LATF crystals. The second harmonic generation (SHG) analysis showed 2.5 times than standard KDP for pure LATF and 2.2, 2.07 times than KDP for urea and thiourea doped LATF.

Renuka et al. (2014) they presented pure and metal substituted L-Polonium Tri Chloro Acetate (LPTCA) single crystals were grown by slow evaporation method. The grown crystals were subjected to single crystal X-ray diffraction (XRD), powder X-ray diffraction, FTIR, UV-Vis.-NIR, hardness, photoluminescence and dielectric studies. The dopant concentration in the crystals was measured by Inductively Coupled Plasma (ICP) analysis. Single crystal X-ray diffraction studies of the pure and metal substituted LPTCA revealed that the grown crystals belong to the trigonal system. Ni^{2+} and Co^{2+} doping slightly altered the lattice parameters of LPTCA without affecting the basic structure of the crystal.

Vijayan et al. (2013) they presented the title compound of iminodiacetic acid hydrochloride (IDAAMHCL) has been successfully synthesized by adopting conventional chemical reaction and the single crystals have been grown by solvent evaporation method at room temperature and studied its various properties and reported for the first time. The lattice dimension and the crystal structure were identified from the powder X-ray

diffraction analysis. The crystalline perfection assessed by high resolution X-ray diffraction technique shows that the specimen is free from structural grain boundaries. The presence of functional groups and the protons in IDAAMHCl was confirmed by Fourier transform infra-red and NMR (1H and 13C) spectroscopic techniques.

Surekha et al. (2014) Optical quality bis glycine hydro bromide (BGHB) single crystal was grown by slow evaporation technique. The third order nonlinear refractive index and nonlinear absorption coefficient of the grown crystal were measured by Z-scan studies. The third order nonlinear susceptibility was found to be 9.612 X 10^{-4} esu which was fairly higher than the other glycine compounds. The Photoluminescence spectra reveal the emission bands for BGHB crystals. The band gap energy was calculated to be 3.1 eV. The Photoconductivity studies were employed to determine the dependence of photocurrent on the applied electric field. Negative photoconductivity was exhibited by the sample. The D.C. conductivity of the grown crystal was measured by the complex impedance analysis wherein the obtained plot in the form of semicircle finds application in Debye relaxation for materials having large D.C. conductivity.

2.3 DOPED TECHNIQUES

2.3.1 Organic Nonlinear Optical Crystal

Priyadharshini and Kalainathan (2017) they presented the bulk organic nonlinear optical single crystal of 2-(2,4-dimethoxybenzylidene)

malononitrile (DMM) with size up to 24 X 18 X 13 mm^3 was successfully grown by slow evaporation solution growth technique. The single crystal X-ray diffraction studies of the grown crystal exhibit that the crystal belongs to a monoclinic system with P 21 space group. The FT-IR spectrum confirms the various functional groups present in the grown crystal. The optical properties of the grown crystals were analyzed by UV–Vis NIR spectral analysis. Third-order nonlinear optical behavior of the title crystal was studied by Z-scan technique.

Zolfagharian and Dizaji (2015) they presented unidirectional <001> $NiSO_4$ doped Tri Glycine Sulphate (TGS) single crystal of 15 mm in diameter and 150 mm in length was successfully grown in aqueous solution by Sankaranarayanan Ramasamy (S-R) method. The characterization of the grown crystal was made by powder X-ray diffraction, UV-Vis. spectroscopy, Fourier transform infrared spectroscopy (FTIR), and Vickers's micro hardness studies. The X-ray diffraction analysis revealed a monoclinic structure for the grown crystal. UV–Vis. analysis showed high transmittance for the doped TGS crystal in the entire visible region. FTIR spectrum verified the presence of various functional groups in the grown specimen. Vickers's micro hardness studies of the doped TGS crystal showed that was harder than pure TGS crystal. The density of the doped crystal was found to be higher than that of the un-doped one.

Kumar et al. (2009) have presented the single crystals of pure; Cu^{2+} and Mg^{2+} doped L-Arginine Acetate (LAA) were grown successfully by slow

evaporation technique. In order to improve the device characteristics of LAA crystals, metal dopants of Cu^{2+} and Mg^{2+} were incorporated into the parent crystals. The grown pure and doped crystals were confirmed by X-ray powder diffraction studies. The pure and doped crystals were characterized by Fourier transform Raman (FT–Raman) and thermal studies. Absorptions of these grown crystals were analyzed using UV–Vis NIR studies, and it was found that these crystals possess minimum absorption in the entire visible region. Nonlinear optical studies of pure and doped crystals were carried out and it reveals that the dopants have increased the efficiency of LAA crystals.

Rajyalakshmi et al. (2015) they presented single crystals of pure and urea doped sulphamic acid single crystals have been grown from aqueous solution by slow evaporation technique. The influence of urea on the growth of sulphamic acid single crystals was characterized by single crystal X-ray diffraction analysis to determine the lattice parameters. The structure of urea doped sulphamic acid single crystals belongs to orthorhombic system. The crystalline perfection was analyzed by high resolution X-ray diffraction studies. Vibrational modes of pure and urea doped was identified using FTIR spectral analysis. UV-visible spectral studies showed that the transmittance of electromagnetic radiation and the lower cut off wavelength was found to be 235 nm. Second harmonic generation measurement indicate that the efficiency of urea doped sulphamic acid single crystals is nearly equal to KDP crystal.

Raja et al. (2017) they presented KDP crystal grown from aqueous solution with Acidic acid which has an organic nonlinear optical material. The

crystal system and cell parameters of grown crystal were determined by single crystal X-ray diffraction analysis. The optical absorption and transmission were examined by UV- Vis analysis which was carried out for the grown crystal. Fourier transform infrared spectroscopy (FTIR) used to confirm the functional group of the crystal. The second harmonic generation (SHG) was tested by Kurtz Perry powder test. Thermal stability was confirmed by TGA/DTA analysis. The mechanical properties of the grown crystal were analyzed and elastic stiffness of a crystal was found by Wooster empirical relation.

Raja et al. (2014) they presented the work of DHA single crystals were successfully grown by the slow evaporation method. Good quality single crystals were harvested after 5 days. The grown crystal was characterized by various techniques namely Single crystal X-ray diffraction, FT-IR, UV–vis, NLO and thermal analysis. The FT-IR analysis confirms the presence of various functional groups available in DHA. The optical transmission study and Kurtz and Perry SHG measurement shows the suitability of doped crystals for NLO applications.

Organic NLO materials have been used for a large number of technological applications in laser sources. **Raja et al. (2017)** they present the work thiourea crystal grown from aqueous solution with Acidic acid which has an organic nonlinear optical material was employed. The cell parameters of the grown crystal were determined by single crystal X-ray diffraction analysis. The optical properties of the crystal were examined by UV- Vis analysis. Fourier transform infrared spectroscopy (FTIR) was used to confirm the functional

group of the crystal. The second harmonic generation (SHG) was tested by Kurtz Perry powder test. The Thermal stability and mechanical properties of the grown crystal were confirmed by TGA/DTA and Vickers's hardness analysis

Uma Maheswari et al. (2010) have presented the thiourea doped L-Threonine (TU doped LT) organic single crystal was grown at room temperature by slow evaporation technique. The lattice parameters and the functional groups are identified by single crystal XRD and FTIR studies respectively. The second harmonic generation (SHG) efficiency of a non-linear optical material was a very important parameter from which they got an idea about the efficiency ofthe material in translating energy from fundamental beam to second harmonic beam. That was confirmed by Kurtz Perry powder technique using Q-switched Nd-YAG laser and the SHG efficiency of the grown crystal was found to be 0.47 times that of urea. That enhances the application of TU doped LT single crystal in non-linear optical applications.

Janarthanan et al. (2011) they presented single crystals of β-Naphtha (βN), an organic nonlinear optical (NLO) material was successfully grown by temperature lowering method using chloroform as solvent. The initial compound was purified by repeated re-crystallization process. As grown crystals were characterized by single crystal X-ray diffraction (XRD) studies to ascertain that βN crystal crystallized in the monoclinic system with a non-Centrosymmetric space group. Vibrational frequencies of various functional

groups in the crystals were derived from Fourier transform infrared (FTIR) spectroscopy and proton nuclear magnetic resonance (NMR) spectrum.

Cao et al. (2011) they presented the Cu-doped hydrogen titanatesnano tubes, they were prepared by hydrothermal process and subsequently ion-exchange reactions. The products were characterized in detail by multiform techniques: X-ray diffraction, scanning electron microscopy, transmission electron microscopy and energy dispersive X-ray analysis. Those tubes are hollow scrolls with a typical outer diameter of 10 to 12 nm, inner diameter of about 6 nm and length of several hundred's nanometers. The photoluminescence and the adsorption properties of Cu-doped hydrogen titanates nanotubes have been systematically investigated.

Zhu et al. (2014) have presented a novel pyridine-containing metal-organic framework (MOF), [Zn (bpdc) DMA]-EDMF, was first constructed by solvo-thermal reaction of bi pyridine, di carboxylate (bpdc) with Zinc nitrate, and then it was converted to nitrogen-doped porous carbons (NPCs) by direct carbonization. The as-prepared porous carbon (NPC800) was characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD), N_2absorption isotherms, and X-ray photoelectron spectroscopy. NPC800 was modified onto glassy carbon electrode surface for investigating its electrochemical applications. Cyclic Voltammetry (CV) and linear sweep voltammetry were performed to evaluate the electro catalytic activity of NPC800 for oxygen reduction reaction (ORR) in alkaline solution. NPC800 exhibited better ORR activity than commercial Pt/C. Pt-catalyst supported on

NPCs (Pt/NPC800) was prepared by means of electro deposition and characterized by SEM, Energy dispersive spectrometry and XRD.

Fang et al. (2014) they presented a series of defect engineered metal organic frameworks (DEMOFs) derived from parent micro porous MOFs was obtained by systematic doping with defective linkers during synthesis, leading to the simultaneous and controllable modification of coordinative unsaturated metal sites (CUS) and introduction of functionalized mesopores. These materials were investigated via Temperature dependent adsorption/desorption of CO monitored by FTIR spectroscopy under ultrahigh vacuum conditions (UHVFTIRS). Accurate structural models for the generated point defects at CUS were deduced by matching experimental data with theoretical simulation. The results reveal multivariate diversity of electronic and steric properties at CUS, demonstrating the MOF defect structure modulation at two length scales in a single step to overcome restricted active site specificity and confined coordination space at CUS.

Anis et al. (2014) they presented a single crystal of L-Cysteine doped Zincthiourea chloride (ZTC) has been grown by slow evaporation technique. The optical study revealed that the doped ZTC crystal has high transmission with lowest cut off wavelength of 306 nm. The optical band gap was found to be 4.2 eV. The transition band gaps were studied using the photoluminescence spectrum. The incorporation of L-Cysteine in ZTC was estimated qualitatively by FT-IR analysis. The presence of dopant was confirmed by energy diffraction X-ray analysis (EDAX) analysis. The lower dielectric characteristics of doped

ZTC crystal were scrutinized by dielectric measurements. The high thermal stability of grown crystal was ascertained by TG/DTA analysis. The Second harmonic generation (SHG) efficiency measured using Nd-YAG laser is 1.96 times that of pure ZTC.

Wang et al. (2016) they compared to extensively studied oxygen reduction reaction (ORR) catalysis in alkaline media, development of highly active and stable non precious metal catalysts (NPMCs) to replace Pt in acidic electrolytes remains grand challenges. Among currently studied catalysts, the Fe-N-C formulation holds the greatest promise for the ORR in acid. Here, we report a new highly active and stable Fe-N-C catalyst featured with well-dispersed atomic Fe in porous carbon matrix. It was prepared through one single thermal conversion from Fe-doped ZIF-8, a metal–organic framework (MOF) containing Zn^{2+} and well-defined $Fe–N_4$ coordination. Unlike other Fe-N-C catalyst preparation, no additional tedious post-treatments such as acid leaching and the second heating treatment are required in this work. Notably, an O_2-free environment for preparing the Fe-doped ZIF-8 precursor is found to be crucial for yielding uniform Fe distribution into highly porous N-doped carbon matrix.

Xie et al. (2015) have presented a novel white-light-emitting organic molecule, which consists of carbazolyl- and phenothiazinyl-substituted benzophenone (OPC) and exhibits aggregation-induced emission-delayed fluorescence (AIE-DF) and mechanofluoro chromic properties was synthesized. The CIE color coordinates of OPC were directly measured with a

non-doped powder, which presented white-emission coordinates (0.33, 0.33) at 244 K to 252 K and (0.35, 0.35) at 298 K. The asymmetric donor–acceptor–donor' (D-A-D') type of OPC exhibits an accurate inherited relationship from dicarbazolyl-substituted benzophenone (O_2C, D-A-D) and di phenothiazinyl substituted benzophenone (O_2P, D'-A-D').

Chandra et al. (2014) they presented two new chemically stable functional crystalline covalent organic frameworks (COFs) (TpAzo and Tp-Stb) were synthesized using the Schiff base reaction between tri-formyl phloroglucinol (Tp) and 4,4′ azodianiline (Azo) or 4,4′ diaminostilbene (Stb), respectively. Both COFs showed the expected keto-enamine form, and high stability toward boiling water, strong acidic, and basic media. H_3PO_4 doping in Tp-Azo leads to immobilization of the acid within the porous framework, which facilitates proton conduction in both the hydrous ($\sigma = 9.9 \times 10^{-4}$ S cm^{-1}) and anhydrous state ($\sigma = 6.7 \times 10^{-5}$ S cm^{-1}).

Anis et al. (2015) they presented optically transparent formic acid (FA) doped potassium di-hydrogen phosphate (KDP) crystal of dimension 21 X 15 X 9 mm^3 has been grown by slow evaporation solution technique (SEST). The X-ray diffraction (XRD) technique was used to confirm the cell parameters and the shifts in peak positions of identified reflecting planes. The incorporation of FA in KDP has been qualitatively analyzed by Fourier transform infrared analysis. The UV-Visible absorption spectrum of crystals has been recorded in the range of 200 nm to 900 nm and the doped KDP crystal was found to have improved optical parameters than pure KDP. The color centered

photoluminescence emission spectrum of grown crystal has been illustrated in visible region. The mechanical behavior of pure and doped KDP crystal has been investigated using the Vickers's micro hardness analyzer and hardness parameters have been calculated.

Zhang et al. (2015) they presented two lanthanide zeolite-like metal-organic frameworks (Ln-ZMOFs) with rho topology, Tb-ZMOF and Eu-ZMOF, were constructed by self-assembly of a 4-connected lanthanide molecular building block (MBB) and a bi-pyridine-di-carboxylate ligand. Varying the Tb^{3+} and Eu^{3+} ratio during synthesis afforded three mixed crystal iso-structural MZMOFs with variable Eu: Tb stoichiometry. Fluorescent studies revealed that a methanol suspension of one of these mixed crystals, MZMOF-3 exhibits selective detection of lyso-phosphatidic acid (LPA), a biomarker for ovarian cancer and other gynecologic cancers.

Kory et al. (2014) they rise of grapheme, a natural two-dimensional polymer (2DP) with topologically planar repeat units, has challenged synthetic chemistry, and has highlighted that accessing equivalent covalently bonded sheet-like macromolecules has, until recently, not been achieved. Here we show that non-Centro symmetric, enantiomorphism single crystals of a simple-to-make monomer can be photo chemically converted into chiral 2DP crystals and cleanly reversed back to the monomer. X-ray diffraction established unequivocal structural proof for this synthetic 2DP, which has an all-carbon scaffold and can be synthesized on the gram scale. The monomer crystals are highly robust, and they can be easily grown to sizes greater than 1 mm and the

resulting 2DP crystals exfoliated into nanometer-thin sheets. This unique combination of features suggests that these 2DPs could find use in membranes and nonlinear optics.

Hotta et al. (2013) they described various single crystal growth methods that produce different morphologies and geometries of crystals. Using these single crystals they highlight construction and performance of the devices. The single crystal approach not only allows us to study the device performance that reflects the intrinsic nature of the organic semiconductors but also is advantageous to enhancement in the steady device operation. A current-injected laser oscillation in an electronic device configuration remains as a big challenge to be achieved.

Because of long-range order and high chemical purity, organic crystals have exhibit unique properties and attracted a lot of interest for application in solid-state lasers. As optical gain materials, they exhibit high stimulated emission cross section and broad tunable wavelength emission as similar to their amorphous counterpart; moreover, high purity and high order give them superior properties such as low scattering trap densities, high thermal stability, as well as highly polarized emission. As electronic materials, they are potentially able to support high current densities, thus making it possible to realize current driven lasers. **Fang et al. (2014)** they described recent research progress in organic semiconductor laser crystals.

J. Uma Maheswari et al (2016) they presented the single crystals of pure lauric acid (LA) were harvested from ethanol solution by a slow evaporation technique. X-ray diffraction showed that the LA crystallized in the monoclinic system and was used to determine the lattice parameters. The Kurtz–Perry powder technique showed that the second harmonic generation efficiency of LA was 0.87 times that of potassium di-hydrogen phosphate. Fourier transform infrared spectral analysis was used to identify the various fatty acid functional groups present in the sample. Thermo gravimetric analysis and differential thermal analysis revealed that the LA crystal was stable up to 45°C. The mechanical strength of the sample crystal was estimated by the Vickers hardness test. Impedance analysis was carried out for the sample at different frequencies and a NY Quist plot was drawn to understand the electrical properties.

2.3.2 Inorganic NLO Crystal

Acetone in the human breath is a crucial biomarker for the clinical diagnosis of diabetes in a noninvasive manner. Traditional methods of breath analysis have some major technical problems and limitations. Xiao et al. (2014) they presented C-doped WO_3 materials are synthesized via a facile cotton fiber-templating route following by calcination. The phase and morphology of the resulting material were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectra and high resolution transmission electron microscopies (HRTEM). The as-fabricated sensors based on C-doped WO_3 materials show fast response and recovery toward acetone

gas down to 0.2 ppm with a well-defined relationship between the concentration and detection response at an operating temperature of 300°C. Upon exposure to methanol, ethanol and NH_3, only slight responses were observed at the same temperature, indicating an excellent selectivity.

Zhang et al. (2015) they presented Tb^{3+}/Yb^{3+} co-doped α-$NaYF_4$ single crystals with various Yb^{3+} concentrations and ~0.40 molar % Tb^{3+} are grown by Bridgman method using KF (Potassium fluoride) as flux with a temperature gradient of 70 °C/cm – 90 °C/cm across the solid liquid interface. The effect and mechanisms of KF in the growing process are studied. The crystal structure is characterized by means of XRD. The high transmission from 300 nm to 7350 nm and maximum phonon energy about 390 cm^{-1} for the α-$NaYF_4$ single crystal are obtained from the measured transmission and Raman spectra, respectively. The luminescent properties of the crystals are investigated through excitation, emission spectra, and decay curves. Down conversion with emission of two near infrared photons about 1000 nm for each blue photon at 486-nm absorption is obtained in Tb^{3+}/Yb^{3+} co-doped α-$NaYF_4$ single crystals. Moreover, the energy transfer processes is studied based on the Inokuti–Hirayama model from the measured luminescent decay curves, and the results indicated that the interaction between Tb^{3+} and Yb^{3+} is electric dipole–dipole.

Mgalan et al (2013) they presented single crystals of pure ADP, pure KDP $CuS0_4$ doped KDP crystals have been grown by slow evaporation solution growth technique. The cell parameters were characterized by powder X-ray diffraction analysis. The enhancement in transmittance of grown pure

ADP or KDP with addition of $CuS0_4$ was determined by UV-Visible spectral analysis.

Douissard et al. (2014) they presented the growth of LuAP single crystalline films on undoped (YAP) by the vertical dipping isothermal Liquid Phase Epitaxy (LPE) growth method. For the comparison of the light output of Ce and Tb doped LuAP SCF screens both cathode-luminescence (CL) and X-ray excited luminescence (RL) measurements were used. For investigations of Ce-Tb energy transfer in the afore mentioned oxide hosts, in addition to using traditional spectroscopic methods, they made time-resolved luminescent spectroscopy of Ce-Tb doped LuAP SCFs under excitation by pulsed synchrotron radiation at the Super-luminisation (HASYLAB at DESY). Recently we have demonstrated the strong quenching influence of flux related impurity on the emission in the Ce-doped LuAP SCF screens. However their present investigation shows that Tb-doped LuAP SCFs are efficient X-ray scintillators, whose light output can be significantly increased by co-doping with ions. Namely, we demonstrate the efficient energy transfer in LuAP: Tb,Ce SCFs.

Fedorov et al. (2016) they studied the radiation resistance of $BaF_2:Ce^{3+}$ scintillator single crystals and ceramics at gamma doses from 106 to 108 rad. It has been shown that the ceramics produced using the self-fluorinating precursor $BaF_2 \cdot$ HF is more radiation-resistant.

Kaczmarek et al. (2014) they presented microstructures of Y_2WO_6 were prepared by applying a hydrothermal synthesis in the presence of sodium dodecyl sulfate (SDS) surfactant, after which the materials were heat-treated at a temperature of 1100 °C. When prepared at pH 3, the spherical 3D microstructures were built from nanosized particles. Raising the pH gave materials built from differently shaped building blocks, which influenced the final architecture. These materials, similarly to other previously investigated and reported rare-earth tungstate materials, were found to show very interesting luminescence properties. However, quantum yield (QY) values have scarcely been reported for such materials. In that work, a detailed study of the photoluminescence characteristics, decay times, and quantum yields of Y_2WO_6 doped with Sm^{3+}, Eu^{3+}, and Dy^{3+} was presented. When doped with different concentrations of Ln^{3+} ions, the luminescence properties of the samples changed. The 2.5% Dy: Y_2WO_6 sample gave white-light emission and showed a QY of 17%.

Kamada et al. (2016) they presented the 3 inch size Mg co-doped Ce: $Gd_3A_{l2}Ga_3O_{12}$single crystals were prepared by the Czochralski (Cz) method. Absorption and luminescence spectra were measured together with several other scintillation characteristics, namely the scintillation decay and light yield to reveal the effect of Mg co-doping. The timing resolution measurement for a pair of 3 X 3 X 3 mm^3 size GAGG:Ce.Mg scintillator crystals were performed using Si-PMs.

Kaur et al. (2016) they presented behavior displayed by samarium doped $LaAlO_3$ phosphor which was synthesized by solid state reaction method. For synthesis of $LaAlO_3$ with variable concentration of Sm (0.2 to 2.5 mol %) phosphor was calculated at 1000 ^{0}C and sintered at 1250 ^{0}C following intermediate grinding. Synthesized sample was characterized by X-ray diffraction analysis and crystallite sized was calculated by Scherer's formula. Surface morphology was determined by scanning electron microscopy technique and it shows good morphology and compact distribution. From PL spectra of prepared phosphors shows broad excitation peak at 250 nm and emission at 566 nm, 600 nm and 608 nm is obtained. The phosphor is prepared by high temperature synthesis method. Twopeaks are obtained in the TL glow curve for lower concentration of Samarium. Single prominentpeak is obtained with further increase in the concentration of dopant. It is characteristic yelloworange emission for samarium ion. The excitation spectra of $LaAlO_3:Sm^{3+}$ phosphor mainly consists of the charge transfer and (CTB) of Sm^{3+} located in 220 to 340 nm centered at 250 nm.

Khan et al. (2016) they presented the crystals of 0.02 %, 0.05 %, 0.1 %, and 0.5 % Sn doped LiI are grown by the vertical Bridgman technique. The luminescence and scintillation properties of the grown crystals are investigated. X-ray excited emission spectrum of LiI (Sn) showed a broad emission band between 400 to 650 nm wavelength ranges at room temperature. Such emission is attributed to Sn^{2+} ion. Scintillation properties such as energy resolution, decay time profiles, and light yield are measured under 662 keV (137Cs) γ-ray

excitation at room temperature. A maximum light yield of 6000 ± 600 pH/MeV is measured at room temperature. LiI (Sn) single crystals showed two exponential decay components under γ-ray excitation. The dependence of scintillation properties on the temperature was also presented.

Leto et al. (2014) they presented the single crystals and nano powders of $LuPO_4$ doped with 1 molar % Pr^{3+} have been synthesized using flux growth and co-precipitation techniques, respectively. The Nanocrystalline powders have been thoroughly characterized from a structural and morphological point of view. The photoluminescence and cathode-luminescence spectra of the two materials have been measured. The spectra evidence both 5d–4f and 4f–4f emission bands located in the UV and visible regions; the relative intensities of the former are reduced in the Nanopowders. This behavior is attributed to surface quenching effects. The decay curves of the Nanopowders relative to the 4f–4f transitions also appear to be affected by quenching with respect to their counterparts in the single crystal.

Ma et al. (2011) they presented the Large-scale cadmium telluride (CdTe) ultra-long single-crystalline micron-size wires were prepared by simple thermal evaporation of a mixture of CdTe and Bi powder. The wires were characterized by X-ray diffraction, energy-dispersive X-ray spectroscopy, scanning electron microscopy, transmission electron microscopy (TEM) and high-resolution TEM. The CdTe wires have a length of up to about 400 mm and diameter of 0.5 to several micrometres. They were found to be single crystalline of Zinc blende phase. The growth of CdTe wires was explainedby

the vapor–liquid–solid mechanism. The as-prepared CdTe micron wires have a narrow photoluminescence peak at 778 nm.

Monika et al. (2014) they presented a series of Dy^{3+} (0.005 to 0.09 molar %) and Li^{+} (0.005 to 0.03 molar %) co-doped strontium cerate(Sr_2CeO_4) Nanopowders are synthesized by low temperature solution combustion synthesis. The effects of Li^{+} doping on the crystal structure, chemical composition, surface morphology and photoluminescence properties are investigated. The X-ray diffraction results confirm that all the samples claimed at 900 ^{o}C show pure orthorhombic phase. Scanning electron microscopy analysis reveals that particles adopt irregular morphology and porous nature of the product. Room temperature photoluminescence results indicate that the phosphor can be effectively excited by near UV radiation (290 to 390 nm) which results in the blue (484 nm) and yellow (575 nm) emission.

Rooh et al. (2014) they presented a new single crystals of Ce-doped are investigated under X-ray and X-ray excitation. These scintillation crystals are grown by two zone vertical Bridgman technique and belong to elpasolite crystal family. Energy resolution, scintillation light yield, non-proportionality, energy resolution as a function of X-rays energies and scintillation decay time measurements Ce^{3+} related X-ray excited emission is observed between 360 and 450 nm wavelength region at room temperature. At higher Ce-concentration both self-trapped excitation (STE) and emissions are disappeared and enhance emission. Less than 662 keV X-rays excitation, shows an energy resolution of 5.2%, (FWHM) at 1% Ce concentration. Best energy resolution of

4.8% (FWHM) is obtained for 10% Ce concentration. No significant improvement is observed in the energy resolution of with the increase of Ce concentration. The highest light yield of about 21,000 pH / MeV is obtained for 10% Ce doped crystal. At room temperature three decay time components are found under -ray excitation for all Ce doped samples. This material is highly hygroscopic.

Thilakavathi et al. (2016) they presented Single crystals of pure and L-Threonine-doped Thiourea, an organic nonlinear optical (NLO) material, were grown by slow evaporation technique at room temperature. The structure of the grown crystals was confirmed by powder X-ray diffraction analysis and the crystals belong to the orthorhombic structure. The UV-Vis-NIR study was performed to reveal the optical behavior of the grown crystals. The UV cut-off wavelength for the pure, 1 and 3 molar % LT-doped Thiourea crystals were found to be 295 nm. The bonding structure and molecular associations due to chemical reactions were analyzed and also the functional groups present in the crystals were identified using FTIR spectrum. Kurtz–Perry powder technique employing Nd: YAG laser was utilized to find the second harmonic generation efficiency of the grown pure and doped crystals which are found to be comparable to that of KDP.

Vinnik et al. (2014) they presented Ti-substituted barium hexferrite $BaFe_{12}O_{19}$ single crystals $BaFe_{12-x}Ti_xO_{19}$ with x up to 1.3 and sizes 2 to 8 mm were grown by spontaneous crystallization from molten sodium carbonate flux. The distribution of Ti on different crystallographic sites was determined from

single crystal X-ray diffraction data. For low Ti contents up to x = 0.8 the unit cell expands; on further increase of the Ti amount the unit cell starts to shrink. This behavior for low Ti contents is most likely due to a reduction of Fe^{3+} to $Fe^{2+}$for charge balance. At higher Ti concentrations, supposedly vacancies in the transition metal substructure are formed. An increasing Ti concentration results in a monotonous reduction of the Curie temperature from 452 to 251 °C and the saturation magnetization at room temperature from 64.8 to 24.8 emu/g for powder samples and from 70.0 to 60.1 emu/g for single crystals (for x up to 0.78).

Tu et al. (2014) they presented the sensitive and selective bio-detection is essential for many applications in biology and medicine, including protein purification, DNA immunoassay, early cancer diagnosis and therapeutics. Lanthanide-doped inorganic Nano probes, emerging as an alternative to conventional molecular luminescent probes by overcoming their current limitations, have attracted a reviving interest for a variety of bio-applications due to their distinct optical properties. In this review, we focus on the most recent progress on the development of lanthanide-doped luminescent Nano-bio-probes and their bio-detection of model analyses, nucleic acids, ions, and disease markers both in vivo and in vitro. In particular, we highlight the typical bio-conjugation strategies and detection techniques for different target analyses. Finally, some most important emerging trends and future efforts toward this rapidly growing field are also proposed.

Ytterbium (Yb) doped rare-earth garnet $Y_3Ga_5O_{12}$ (YGG) single crystal was grown by the optical floating zone method for the first time, to our knowledge. Its structure and cell parameter were determined by X-ray powder diffraction. The thermal properties of Yb:YGG, including specific heat, thermal expansion coefficient, thermal diffusion coefficient, and thermalconductivity, were investigated by **Yu et al. (2010).** The optical properties of thecrystal were also studied and the effective gain cross sections were calculated. With the crystal cut along the (111) direction, laser performance was also demonstrated by using a laser diode as the pump source.

Zhang et al. (2014) they presented giant bipolar and unipolar strains i.e. $S_{max} > 0.5\%$, $e_{max}/E_{max} > 1000$ pm V^{-1} have been observed in Mn-doped $Na_{0.5}Bi_{0.5}TiO_3$–$6BaTiO_3$ single crystals after being annealed. Temperature-dependent impedance spectra were studied and activation energies of oxygen vacancies were calculated accordingly. The two different binding energies present in X-ray photoelectron spectra for Na and Bi were assigned to different coordinate environments. However, titanium exhibits only one oxidation state (e.g. Ti^{4+}). The site occupation and valence fluctuation of Mn were characterized by electric paramagnetic resonance spectra.

2.3.3 Semi Organic NLO crystal

Prasanna et al. (2014) they presented a semi organic crystal triglycine Zinc chloride and Magnesium doped triglycine Zinc chloride were grown by solvent evaporation method. The pure and doped TGZC single crystals were

subjected to structural and optical analysis. From the powder XRD studies it was found that TGZC and Magnesium doped TGZC belong to orthorhombic crystal structure with Pbn_{21} space group. It is seen that both pure and doped TGZC are transparent over the entire range of UV- Visible region and the cut off was found to be 228 nm. With the increase in the doped percentage from 0.1 to 0.3 there was a decrease in the absorbance which shows that there was an increase in the transmittance. Thus addition of Magnesium has increased the transmittance of the TGZC which was very essential for a good NLO crystal.

Ganaraj et al. (2017) they presented the single crystal of glycine doped sodium chloride, a semi organic non-linear optical material has been grown from solution (pH = 6) by slow evaporation at room temperature. The expected functional groups of the title compound were confirmed by the FTIR spectral analysis. The crystalline nature and its various planes of reflections were observed by the powder XRD. The optical quality of single crystal of glycine doped sodium chloride identified by UV visible studies.

Venus et al. (2015) they have grown PLA single crystal by slow evaporation method. The lattice parameters were calculated from single crystal XRD data. XRD analysis yielded a space group of $P2_1$ with lattice parameters a = 10.470 Å, b = 8.839 Å, c = 12.808 Å, $\alpha = \beta = 90° \neq \gamma$, volume = 1185.30 $Å^3$. Solubility studies were made at different temperatures with various solvents. The solubility was found to be 17 g in 100 ml of water at room temperature. The functional groups present in the grown sample were identified from the vibrational frequencies of the recorded FTIR spectrum. UV–Vis-NIR

spectrum of PLA crystal shows the cut off wavelength of the crystal to be at 230 nm. The second harmonic generation efficiency of PLA single crystal estimated using Kurtz and Perry method. The nature of variation of dielectric constant (ε_r) and dielectric loss (D) with frequency at different temperatures were investigated.

Bamini et al. (2015) they presented the dye-doped KAP crystals with different dye concentrations such as 0.01 mMolar, 0.03 mMolar, 0.05 mMolar, 0.07 mMolar and 0.09 mMolar (in the KAP growth solution) were grown. The linear optical, non-linear optical, mechanical and thermal characterizations of dye-doped KAP crystals were studied and compared to understand the effect of dye and dye concentration on the KAP crystal. Absorption and emission studies of KAP and dye-doped KAP single crystals indicated the inclusion of the dye into the KAP crystal lattice. The effect of dye and its concentration on the SHG efficiency of the KAP crystal was studied using the Kurtz and Perry powder technique. It was observed that the absorption maximum wavelength and concentration of the dye used for doping the KAP single crystal decided the SHG efficiency of the dye-doped KAP single crystals.

Rasal et al. (2017) they Optically transparent 11 X 10 X 4 mm^3 Bis-Thiourea Zinc Chloride (BTZC) doped Potassium Di-hydrogen Phosphate (KDP) crystal has been grown by slow evaporation solution technique. The cell parameters of the grown crystal have been determined by single crystal X-ray diffraction analysis. The incorporation of BTZC in KDP crystal has been qualitatively analyzed by FT-IR spectral analysis. The optical transparency and

vital optical constants of BTZC doped KDP single crystals have been evaluated in the range of 200 to 900 nm. The mechanical behavior of pure and doped KDP crystals has been investigated under the Vickers microhardness studies. The dielectric parameters of grown crystal have been investigated within the frequency range of 10 to 100 kHz. In Kurtz–Perry powder test, thesecond harmonic generation (SHG) efficiency of BTZC doped KDP crystal was found to be 1.65 timesthat of KDP material.

Peter and Ramasamy (2016) have presented the single crystals of tri-glycinium calcium nitrate, a semi organic nonlinear optical (NLO) material; have been grown by slow solvent evaporation technique at room temperature. The size of the grown crystal is up to the dimension of 29 X 19 X 5 mm^3. The structure of the crystal was analyzed by single crystal X-ray diffraction and the functional groups present in the sample were identified by FTIR spectral analysis in the range 4000 to 450 cm^{-1}. The UV-Vis NIR studies was undertaken to find the transmittance in the ultraviolet and visible region. The efficiency of second harmonic generation was analyzed by Kurtz Perry powder technique and compared with standard KDP crystal. Thermo-gravimetric and differential thermal analysis have been performed to determine the thermal stability of the crystal. Dielectric properties such as dielectric constant and dielectric loss were studied at various temperatures and frequencies. Vickers microhardness testing was carried out on the as grown crystal surface to reveal the mechanical properties of the crystal. Etching

studies were made on the as grown crystal to analyze the structural imperfection of the crystal.

Anandan et al. (2014) have presented the single crystals of pure and potassium halides additive mixed l-arginine phosphate monohydrate have been grown with good optical quality by slow temperature reduction method. Microbial growth aspects and coloration have been studied on the growth solutions. In addition to that the structural properties have been studied by powder X-ray diffraction method and Fourier transforms infrared spectral analyses for the grown crystals. Thermal stability of the grown crystals were studied by thermo gravimetric (TG) and differential thermal analyses (DTA) and found that the grown crystals are suitable for device fabrication for frequency conversion applications.

Niraimathi et al. (2015) they investigated the influence of dopant Mg^{2+} on the growth process, crystalline properties of potassium acid phthalate (KAP). Powder X-ray diffraction (XRD) and inductively coupled plasma-optical emission spectrometry (ICP-OES) studies confirmed the Mg^{2+} ion doping into KAP crystals. The modes of vibration in the crystal lattice have been determined by Fourier Transform Infrared (FTIR) analysis. Optical transmission studies were carried out by allowing the UV-NIR ray of wavelength between 190 nm and 1000 nm, which is to pass through the (010) face of the grown KAP crystals and the results confirm thatboth the pure and doped KAP single crystal shows good transparency in the entire visible region, which is suitable foroptical device applications.

Gandhimathi et.al (2015) they presented a new semi-organic non-linear optical crystal of Manganese Sulpho Tartrate (MST) has been grown successfully by slow evaporation technique. The grown crystals were transparent and pink in color. The solubility study has been carried out in the temperature range 30 to 50 °C in de-ionized water. The lattice parameters of the grown crystals were determined by single crystal X-ray diffraction technique and the crystalline nature of the grown crystal was confirmed by powder XRD analysis. The presence of the functional groups in the crystal lattice was confirmed by Fourier Transform Infra-Red spectral analysis. The UV–Vis-NIR spectrum of MST shows good transmittance in the visible region which enables it to be suitable for optical applications.

Ilayabarathi et al. (2013) have presented a semi-organic crystal of L-Tyrosine Hydrochloride; having dimensions up to (7 mm X 5 mm X 3 mm) has been grown by slow evaporation technique. The grown crystal was characterized by CHNS, UV visible study and DSC analysis. The lower cut off wavelength of grown crystal was below 300 nm and has a wide transparency window, which is suitable for second harmonic generation. Photoluminescence study was also carried out. DSC analysis confirms that the crystal is stable up to 240 ˚C. The dielectric measurement of the crystal was studied as function of temperatures with three different frequencies. Photoconductivity of the sample revealed its positive photoconductivity nature. The second harmonic generation efficiency of crystal was tested by modified Kurtz–Perry powder technique.

Jayanthiand Thamizharasan (2017) have presented a semi organic singlecrystal of DL-Methionine doped Copper Sulphate has been grown by slow evaporation solution growth technique. Lattice parameter of the grown crystal was confirmed by single crystal X-ray diffraction analysis. Vickers's microhardness indentation tests were carriedout with the load ranging from 10 to 100gm. Mechanical parameters like fracture toughness (Kc), brittleness index (Bi), yield strength (σ_y) and elastic stiffness constant (C11) were calculated and reported.

Selvaraju et al. (2012) have presented a new semi organic nonlinear optical Thio Semi Carbazide Cadmium Acetate (TSCA) material has been synthesized. TSCA single crystals were grown from aqueous solution by slow evaporation method. The solubility of TSCA has been determined for various temperatures. The grown crystals were characterized by single crystal X-ray diffraction (XRD), FTIR, UV Vis., thermal and second harmonic generation (SHG) analysis. Single crystal XRD study has been carried out to identify the lattice parameters. FTIR studies confirm the functional groups present in the grown crystal. Optical transmission studies have confirmed that the grown crystal is highly transparent. Thermogravimetric and differential thermal analyses reveal the good thermal stability of the material. The SHG conversion efficiency of TSCA was determined using Kurtz powder technique and found two times that of potassium di-hydrogen orthophosphate (KDP).

Kanchana et al. (2013) they presented the trivalent metal ion (Al, Cr, Fe) doped potassium hydrogen phthalate (KAP) crystals have been grown from

aqueous solution at room temperature. Powder XRD and ICP-OES studies confirmed the metal ion doping into KAP crystals. The presence of functional groups in the crystal has been observed by FTIR analysis. Optical transmission studies were carried out by allowing the UV-NIR ray of wavelength between 190nm and 1000 nm to pass through the (010) face of the grown KAP crystals. Dielectric constant value of Fe-doped KAP at 100 Hz was found to be significantly higher than that of undoped and Cr and Al doped KAP. TG DTA studies show the decomposition temperatures to be 255 ^{0}C, 270 ^{0}C, 258 ^{0}C and 287 ^{0}C for pure, Al^{3+}, Cr^{3+} and Fe^{3+} doped KAP crystals respectively.

Kumaresh and Kumar (2013) they presented the potassium di hydrogen phosphate (KDP) is an efficient nonlinear optical crystal employed in frequency conversion applications. 1 mole % hip uric acid doped potassium di hydrogen phosphate (HAKDP) crystals with the dimensions 35 X 8 X 4 mm^3 were grown using the slow evaporation technique. The grown HAKDP crystal was iso structural with pure KDP, but a variation in the crystallographic parameters was observed. The UV-VIS-NIR study suggests that the crystal is highly transparent in the region 340 to 1200 nm. The functional groups present in the grown crystal were observed in the FTIR analysis. The powder SHG test performed on the grown crystal revealed the NLO efficiency of the crystal has increased due to doping when compared with pure KDP crystal.

Vijaya and Sagunthala (2014) they presented mechanical, dielectric, FTIR and UV studies of Single crystals of Manganese (II) Sulphate doped with

basic amino acid L-Lysine HCl crystals have been studied and compared. Vickers's micro hardness test was carried out to study the mechanical strength of the crystals. The Meyer's index number (n) was calculated using Vickers's micro hardness number. The change in concentration of L-Lysine brings an impact on the mechanical strength of the crystals. The dielectric constant and dielectric loss were found to decrease when the frequency is increased. Low dielectric constant and dielectric loss at higher frequency is a desirable property to enhance the SHG efficiency. Fourier transform infrared spectroscopy study confirms the incorporation of L-Lysine into $MnSO_4$ crystal.

Samuel et.al (2014) they presented the single crystals of pure and L-Aspartic acid doped Zinc (Tris) ThioureaSulphate (ZTS) were grown from aqueous solution by solution growth method. The cell parameters and structure of the grown crystals were determined by X-ray diffraction studies. The presence of functional group in the compound has been confirmed by FTIR and FT-Raman analysis. The optical transparency range has been studied through UV–Vis spectroscopy. TGA/DTA studies show thermal stability of the grown crystals.

Saravanan et al. (2016) Effects of the addition of semi organic NLO materials potassium hydrogen malate monohydrate (PHMM) and sodium acid phthalate (NaAP) on the growth and various properties of ammonium di-hydrogen phosphate (ADP) single crystal grown by the slow cooling method have been studied. The metastable zone width of pure and doped ADP were determined and compared. Nucleation studies shows that metastable zone

width and growth rate of ADP are enhanced by the dopants PHMM and NaAP. The grown crystals were subjected to Powder XRD, FT-IR, UV–Vis, TG/DSC, micro hardness and dielectric studies. Thegrown crystal has good optical transparency in the entire visible region, which was an essential requirement for a nonlinear crystal. Dielectric measurements reveal that doped ADP crystals have low dielectric loss and higher dielectric constant than pure ADP. The relative SHG efficiency measurements revealedthat the dopant has enhanced the efficiency. Presence of dopant was confirmed by energy dispersive spectrometry.

2.4 Dielectric Studies

Delci Zion et al. (2013) they presented Single crystals of pure and boron doped ammonium di-hydrogen phosphate were grown from aqueous solution by slow solvent evaporation process. ICP studies were done to confirm the presence of the do pant boron in the parent crystal. The values of the lattice parameters were determined by single crystal X-ray diffraction. The pure and doped ADP crystals were found to have tetragonal structure. Complete optical characterizations of the crystals were done using the FTIR, UV-Vis and NLO studies. The presences of the various functional groups in the crystals were identified by FTIR spectrum. The band gap energies of the pure and doped crystals have been calculated at their cut off frequencies using the UV-Vis spectrum. The second harmonic generation efficiency of the crystals was determined. The electric properties of the grown crystal have been analyzed by studying the variation of dielectric constant and dielectric loss with frequency.

Ketan D. Parikh et al. (2012) they presented the potassium di-hydrogen phosphate (KDP) is a well-known nonlinear optical (NLO) material having different applications in electro-optics and laser technology. Pure and amino acid L-Arginine doped KDP single crystals were grown by the slow solvent evaporation technique. The 0.3, 0.4 and 0.5 weight % doping of L-Arginine was successfully achieved in KDP crystals and confirmed by paper chromatography, CHN analysis, FTIR and UV-Vis spectroscopes. The dielectric behavior of the samples has been studied. The variation of dielectric constant, dielectric loss (tanδ), a.c. resistivity and a.c. conductivity with frequency of applied field in the range from 100 Hz to 100 kHz is reported. The effect of amino acid doping was observed on SHG efficiency.