CHAPTER 3

LITERATURE SURVEY

The Non Linear Optical (NLO) process requires materials that manipulate the amplitude, phase, polarization and frequency of optical beams.Non Linear optical materials have long been known to interact with light to produce a nonlinear response and the composition of these materials. These types of materials generally fall into one of two classes, either organic or inorganic.

3.1 ORGANIC CRYSTALS

Last two decades, significant efforts have been made in the field of organic nonlinear optical materials because of their potential applications in second harmonic generation, frequency mixing, electro optic modulation and photorefractive properties. Many organic molecules have been reported to have larger nonlinear optical susceptibilities within the 0.5-2.0 µm transparency domain. Organic materials have another advantage that the properties can be optimized by modifying the molecular structure by using molecular engineering and synthesis methods. A very large operating bandwidth modulation in organic electro-optic devices can be obtained through its low dielectric constant at lower frequencies. The organic materials exhibit extremely large nonlinear optical and electro-optic effects. The Electronic nonlinearities are essentially based on the molecular units. Due to the important advantages of the organic materials, they will be widely used in the field of organic chemistry, materials science, physics and electrical engineering. The organic NLO crystals usually have poor mechanical and thermal properties and are susceptible for damage during processing even though they have large NLO efficiency. Also it is very difficult to grow larger size optical-quality crystals of these materials for device applications.

3.2 INORGANIC CRYSTALS

Inorganic crystals are mostly ionic bonded. It is always easier to synthesize inorganic materials. Often, these materials have high melting point and high degree of chemical inertness. High temperature oxide materials are well studied for diverse applications like piezoelectric, ferroelectricity and electro-optics. Some of the useful crystals discovered are Lithium Niobate ($LiNbO_3$), Potassium niobate **(**$KNbO_3$), Potassium Dihydrogen Phosphate (KDP) and its analogues, Potassium Titanyl Phosphate (KTP) and its analogues. Many of these materials have been successfully used in commercial frequency doublers, mixers and parametric generators to provide coherent laser radiation at high efficiency in new regions of the spectrum inaccessible by other nonlinear optical crystal and conventional laser sources. Pure inorganic NLO materials have excellent mechanical and thermal properties, but possess relatively moderate optical nonlinearity.

3.3 SEMI ORGANIC CRYSTALS

In recent years, the need of nonlinear optical materials is much more than other materials (organic and inorganic) because of their applications in optoelectronics and photonics. Materials with large second order optical non1inearities, short transparency cutoff wavelength and stable physico thermal performance are needed in order to realize many of these applications. To overcome these problems in organic and inorganic crystals, the combination of organic and inorganic hybrid compounds leads to find a new class of materials for electronic industries, called semi organic materials. In semi organic materials, the organic ligand is ionical1y bonded with inorganic host, because of their high mechanical strength and chemical stability. The semi organic crystals possess several attractive properties, such as high damage threshold, wide transparency region and high nonlinear coefficient. The contribution from the delocalized π electrons belonging to the organic ligand results in wide optical transmittance and high nonlinear electro optic coefficients. Many NLO based device applications require single crystals in bulk form. This is achieved only by preparing semi organic crystals, which exhibit wide transparency, large and bulk crystals.

3.4 NON LINEAR OPTICAL MATERIALS

In the field of electricity and magnetism, yet nonlinearities are known since scientists have begun to study the phenomena in more detail. Non Linear Optics (NLO) deals with the study of interaction with intense electromagnetic field with materials to produce modified fields that are different from the input field in phase and frequency or amplitude. Second harmonic generation (SHG) is a nonlinear optical process that results in the conversion of an input optical wave into an output wave of twice the input frequency.

However, in the field of optics, nonlinear effects became a subject of interest only after the invention of the laser. As laser physics started with the ruby laser with its high pulse intensities, have many classical experiments in nonlinear optics were successfully performed. Among them second order processes such as second harmonic generation and sum-frequency generation.

The growth of single crystals and their characterizations towards device fabrications are most important in both basic and applied scientific research. Nonlinear optical frequency conversion materials have significant impact on laser technology. However, some special nonlinear optical problems called for crystals with improved properties like high transparency in the UV region, high nonlinearity etc. This leads to the synthesis of new NLO materials of high optical quality.

There is a current interest in finding materials that will extend the wavelength capability of laser sources into UV region and new frequency conversion materials will have significant impact on applications such as optical communications technology and laser driven inertial confinement fusion experiment. This demands from optical and device physicists for improved and effective materials to call for world-wide research on NLO materials which is most targeted and speculative.

3.5 FERRO ELECTRIC MATERIALS

Ferro electricity is a physical property of a material whereby it exhibits a spontaneous electric dipole moment by the application of an external electric field. Ferroelectrics are key materials in microelectronics. Their excellent dielectric properties make them suitable for electronic components such as capacitors, filters etc. Ferroelectric capacitors are used to make ferroelectric RAM for computers. The combined properties of memory devices, piezoelectricity, and pyroelectricity make ferroelectric capacitors as some of the most useful technological devices in modern society.

3.6 APPLICATIONS OF FERROMAGNETIC MATERIALS

In recent years, ferroelectric materials and thin films have attracted much attention and exhibited potential in many important applications such as

- Dynamic random access memories (DRAMS),
- Non-volatile ferroelectric random access memories micro-armours
- Infrared sensors.

- Piezoelectrics for ultrasound imaging and actuators
- Electro-optic materials for data storage applications
- Thermistors
- Switches known as Transchargers or Tanspolarizers
- Oscillators, filters and capacitors
- Light deflectors, modulators and displays

At present, the ferroelectric materials suitable for these devices are $Pb(Zr,Ti)O_3$ (PZT) systems, $SrBi_2Ta_2O_9$ (SBT) systems, $Bi_4Ti_3O_{12}$ (BIT) systems and $BaTiO_3$ (BT) systems that are studied with a great deal of interest. In these ferroelectric materials, $BaTi_{0.91}(Hf_{0.5},Zr_{0.5})_{0.09}O_3$ (BTHZ-9), one of the BT systems, which has several advantages such as

- An extremely low coercive field,
- A high remnant polarization,
- Better mechanical strength and
- Small deviation in composition could have a strong potential application for ferroelectric thin film devices.

General properties of KDP single crystals

Potassium Dihydrogen Phosphate (KDP) is an excellent inorganic NLO material with different device applications. Single crystals of KDP and its isomorphs are representatives of hydrogen bonded materials which possess important piezoelectric, ferroelectric, electro-optic, mechanical and nonlinear optical properties. KDP crystals possess high optical and structural perfection that make it possible to produce elements for doubling and tripling of laser radiation frequency.

KDP is a model system for nonlinear device application therefore it is used as a standard to characterize the nonlinear optical response of other crystal samples. Since the crystal exhibits excellent electro-optical and nonlinear optical properties it is commonly used in frequency conversion applications such as second, third, and fourth harmonic generation, in electro-optical modulation, optical image storage and optical communication. Due to its high electro-optic coefficient large single crystal plates of KDP are widely applied as Q-switches and laser radiation converters for very high energy Nd-glass lasers used for laser inertial fusion experiments. The electro-optic effect in KDP leads to the applications such as polarization filter, electronic light shutter, optical rectifier, electronic light modulator, piezo-optic resonator, transducer etc. They are also used to control the parameters of laser light such as pulse length, polarization and frequency through the first and second order electro-optic effect.

KDP crystal is an efficient angle tuned dielectric medium for the optical harmonic generation in and near the visible region. This material offers high transmission throughout the visible spectrum and meets the requirement for optical birefringence, large enough to bracket the refractive index for even the extreme wavelength over which it is transparent. An additional advantage of KDP is its ability to withstand repeated exposure to high power density laser radiation without inducing strains and subsequent inhomogeneities in the refractive index. These characteristics make KDP a desirable material for frequency doubling and mixing experiments with many solid state and dye lasers with fundamental wavelengths between 1060 and 525 nm.

3.7 COMPARATIVE STUDIES

S. No	Crystal name	Single CrystalXRD			UV-vis-NIR	FTIR Spectrum		Thermal analysis	NLO
		CellPara meters	XRDdatas	Crystal system	Cut off wave Length	Wave number (cm^{-1})	Assignments		
1	L-Valine Magnesium Chloride By(Reena Priya. J et.al)	a (Å) b (Å) c (Å) α (deg) β (deg) γ (deg) Volume(Å^3)	5.434 7.053 10.38 90° 91.63° 90° 397.6	Monoclinic	Occurs at 248 nm. It reveals that the grown crystal is transparent in the UV visible region	2594 629 1483	C-H absorption band C-H in plane bending carboxylic group O – H stretch	weight loss starts at 213°C, it is due to the liberation of vapours like Cl_2, N_2, NH_3,	SHG efficiency is found to be 1.2 times that of KDP
2	L-Histidine Nitrate By (Prakash.P et.al)	a (Å) b (Å) c (Å) α (deg) β (deg) γ (deg) Volume(Å^3)	5.250 7.119 25.04 90° 90° 90° 936.15	Orthorhombic	Lower cut off wavelength at 340 nm.	1630 1133 1089	C=O stretch -ing C-N-C C-O-C	1.the endothermic peak in the DTA curve at 228°C representthe melting point 2. the exothermic peak at 259°C indicates the decomposition of the com-pound	SHG – efficiency is found to be 2.5 times as large as that of KDP
3	L- Histidine Barium Chloride By(Beena T.R. et.al)	a (Å) b (Å) c (Å) α (deg) β (deg) γ (deg) Volume (Å^3)	5.167 7.378 18.93 90° 90° 90° 721.81	Orthorhombic	cut off wavelength of LHBC crystal is 215 nm.	3017 3823 3717	C-H stretch in the ring O-H stretch NH_2 stretch of the amine group	In the DTA trace there was a sharp endothermic peak at 269°C which is the melting point of the crystal.	The SHG efficiency of LHBC is found to be about 0.8 times that of KDP
4	L-Valine Zinc Chloride	a (Å) b (Å)	5.26 9.70	Ortho rhombic	The UV cutoff wavelength was	1328	C–O stretching	weight loss starts at 212° C to 298° C without any	The output power

S. No	Crystal name	Single CrystalXRD			UV-vis-NIR	FTIR Spectrum		Thermal analysis	NLO
		CellPara meters	XRDdatas	Crystal system	Cut off wave Length	Wave number (cm^{-1})	Assignments		
	By(Vivekanandhan. R et.al)	c (Å) α (deg) β (deg) γ (deg) Volume ($Å^3$)	12.00 90° 90° 90° 612		found to be at 230 nm.	1270 947	CH_3 deformation CH_3 rocking	intermediate stages, is assigned as melting point of the crystal.	is found to be greater than that of KDP
5	L-Histidine Tetra fluro borate By(Arockia Avila. S et.al)	a (Å) b (Å) c (Å) α (deg) β (deg) γ (deg) Volume ($Å^3$)	5.022 9.090 10.21 90 93.48 90 467	Monoclinic	direct band gap energy of LHFB is found to be 4.79eV	2800 2862	Symmetric stretching vibration asymmetric stretching vibration	Endothermic peak observed at around 280°C attributed to the melting point of the material	SHG efficiency is 0.48864 times that of KDP
6	L-valineCadmium chloride By(Sheen Kumar. N et.al)	a (Å) b (Å) c (Å) α (deg) β (deg) γ (deg) Volume($Å^3$)	10.28 5.622 12.54 90° 95.76° 90° 721.7	Monoclinic					SHG efficiency is 1.32 times that of KDP
7	Bis glycine Hydro -gen chloride (Ambujam. K et.al)	a (Å) b (Å) c (Å) α (deg) β (deg) γ (deg) Volume($Å^3$)	5.229 8.117 18.06 90° 90° 90° 777.02	Orthorhombic	The cut-off frequency is around 300 nm.	1591 673 628	NH_3^+ asymmetric bend _COO- bend CN stretch	The DTA trace indicates a weak endothermic starting at about 146.8°C which may be assigned to isomorphic transformation, as there is noCorresponding weight loss in TGA trace.	
8	Glycine potassium iodide	a (Å) b (Å)	6.987 6.987	Trigonal	The lower cutoff wavelength of the				

S. No	Crystal name	Single CrystalXRD			UV-vis-NIR	FTIR Spectrum		Thermal analysis	NLO
		CellPara meters	XRDdatas	Crystal system	Cut off wave Length	Wave number (cm^{-1})	Assignments		
	By(Kannan.P.S. et.al)	c (Å) α (deg) β (deg) γ (deg) Volume(Å^3)	5.489 90° 90° 120 230.45		crystal was found to be at 341 nm				
9	Glycine Sodium Nitrate By(Mary. et.al)	a (Å) b (Å) c (Å) α (deg) β (deg) γ (deg)	14.32 5.257 9.115 90° 111.0 90°	Monoclinic	The UV cut off wavelength for the grown crystal is found to be at 310 nm.	2165 1497 1333	N H vibration carboxylate group CH_2 wagging	In TG curve, the weight loss for the sample takes place in two different stages at temperatures of 374°C and 810°C, 1. weight loss occurs at 374° C. 2. exothermic peak is also observed at 420° C	
10	Glycine Magnesium Chloride By(Thaila. T et.al)	a (Å) b (Å) c (Å) α (deg) β (deg) γ (deg) Volume (Å^3)	7.024 7.013 5.479 90° 90° 120° 233.5	Hexagonal	very low cut off wavelength 230 nmalong with a largetransmission window	1384 2837	COO group CH_2 group	It is observed that there is a single stage of weight loss starting at 222° C	SHG efficiency of the crystal was 0.5 times that of KDP.
11	ThioSemicarbazide Zinc Acetate By(Sankar. K et.al)	a (Å) b (Å) c (Å) α (deg) β (deg) γ (deg) Volume(Å^3)	4.93 6.01 7.32 77.04° 77.07° 83.66 205	Triclinic	The lower cut off wavelength is observed at 279 nm.	3371 2968 1312	γ (C-H) stretching CH_2 Vibration of amino acid (C-NH_2) mode of vibration	The TGA curve shows the weightpercentage of about 98.75% observed at 170° C and 60% observed at 240° C	Emission of green radiation confirm the 2nd harmonic generation
12	Triglycine calcium bromide	a (Å) b (Å)	9.095 14.75	Ortho rhombic	The lower cut off region is obtained	1591	COO-asymmetric	In the spectrum of thermo-gravimetric analysis, there	It was observed that

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		CellPara meters	XRDdatas	Crystal system	Cut off wave Length	Wave number (cm^{-1})	Assignments		
	By(Esthaku Peter. M et.al)	c (Å) α (deg) β (deg) γ (deg) Volume ($Å^3$)	20.21 90.34 90.46 90.07 2713		at 240 nm.	670 515 3049	stretch C–Br stretching Ca–O bond NH_3^+ stretching	is no weight loss upto 305ºC	the output voltage was 32.8mV. Hence the SHGefficiency of the crystal is half of that of KDP crystal
13	L-Histidinium Maleate By(Alosious Gonsago. C et.al)	a (Å) b (Å) c (Å) α (deg) β (deg) γ (deg) Volume($Å^3$)	11.46 8.053 14.97 90º 101.6 90º 1353	Monoclinic	From the transmitance spectrum, it is observed that the grown crystal is completely transparent in the UV and visible spectral regions with the lower cut off wavelength around 280 nm			The melting point of the compound is found to be 139° C.	SHG efficiency of L-histidinium maleate is comparable with the standard KDP
14	L – Bis valine Selenate By(Thiru Gnanam. A et.al)	a (Å) b (Å) c (Å) α (deg) β (deg) γ (deg) Volume($Å^3$)	1.11 5.17 13.03 90º 111 90º 696	Monoclinic	The lower cut off wavelength of grown crystal is at 320 nm.	3018 1701 1155	N-H primary amines C=O stretching C-O stretching vibration	There is a sharp weight loss at 259ºC. Below the onset of decomposition, no weight loss is observed and hence the crystal is completely free fromphysicallyobserved water or water of crystallization	The Efficiency is 0.56 times as that of KDP
15	Thio	a (Å)	6.675	MonoClinic	Characterstics	3180	O-H vibration	The first endothermic peak	SHG

S. No	Crystal name	Single CrystalXRD			UV-vis-NIR	FTIR Spectrum		Thermal analysis	NLO
		CellPara meters	XRDdatas	Crystal system	Cut off wave Length	Wave number (cm^{-1})	Assignments		
	Semicarbazide Cadmium Acetate By(Selvaraju. K et.al)	b (Å) c (Å) α (deg) β (deg) γ (deg)	10.5623.96 90° 109.2° 90°		absorbance band only at 280 nm	1534 649	C=S N-H out-of plane bending vibrations	in DTA at 163°Ccorresponds to the phase transformation.	efficiency of the crystal was two times that of KDP
16	Cadmium ThioSemi Carbazide Bromide By(Madeswaran. P et.al)	a (Å) b (Å) c (Å) α (deg) β (deg) γ (deg) Volume($Å^3$)	5.09 6.14 7.53 77.80 77.20 84.00 225	Triclinic	The lower cut-off wave -length was found to be 236 nm	1641 1562 683	NH_2 bending N-C-N asymmetric stretching C-Br stretching.		SHG conversion efficiency of the crystal is 198 mV.
17	Glycine Ammonium Chloride By(Radharamanan. M et.al)	a (Å) b (Å) c (Å)	6.941 6.941 5.419	Hexagonal	The UV cut-off wave-length is found to be at 250 nm	1325 1585	CH_2 twisting mode COO– asymmetric stretching vibration	There is no loss of water below 190˚ C illustrating the absence of absorbedwater and the sharp weight lossat 255˚ C shows the melting point of the crystal.	The SHG efficiency of thegrown crystal was 0.8 times greater that of KDP.
18	Bisglycine SodiumNitrate By(Sankar. R et.al)	a (Å) b (Å) c (Å) α (deg) β (deg) γ (deg) Volume($Å^3$)	14.33 5.265 9.118 90° 119.2° 90° 688.1	Orthorhombic	UV cutoff below 220 nm, which is sufficient for a SHG laser radiation of 1064 nm.	891 1410 1032 1200-1300	NO_3^- group COO^- Symmetric stretch CCN CH_2 twist/	The DTA trace indicates a strong endothermic starting at 272.2°C due to its meltingof the crystal.	SHG efficiency is only0.3–0.4 times that of KDP

S. No	Crystal name	Single CrystalXRD			UV-vis-NIR	FTIR Spectrum		Thermal analysis	NLO
		CellPara meters	XRDdatas	Crystal system	Cut off wave Length	Wave number (cm^{-1})	Assignments		
							NHinplane bending mixing		
19	Thio semicarbazide Cadmium bromide By(Chandrasekaran. J et.al)					3168 1641 1562	NH_2 group Symmetric vibration Vibrational mode N-C-N asymmetric stretching	Exothermic peak noticed at 205° C corresponds to the melting point of the crystal	SHG conversion efficiency of KDP is 105mV and for TSCCB is 198 mV
20	ThioSemi Carbazide Potassium chloride By(Chandrasekaran. J et.al)				UV cut-off below is found to be at 260 nm, which is sufficient for SHG properties	1620 1001 503	NH_2 deformation C–Cl Stretching mode N–C–S Stretching	From the DTA curve it is observed that the material is stable up to 185° C	

The above discussed properties of various single crystal motivated to grow the following crystals.

1. L-valine Ferric Chloride
2. Thiosemicarbazide Manganous Acetate
3. Glycine Manganous Acetate
4. L-Histidine Cadmium Bromide