CHAPTER 7

SUMMARY AND SCOPE FOR FUTURE RESEARCH

7.1 SUMMARY

The design, discovery and growth of novel materials, especially in single crystal form, represent a national core competency that is essential for scientific progress and long-term economic growth. New materials lay at the core of many new and emerging technologies, such as semiconductor electronics, solid state lasers, radiation detectors, compact disk storage, both cellular and optical communications, solar cells, fuel cells and catalysts. Single crystals are often required to achieve a materials' full functionality as well as to completely elucidate its properties. Though research on nano-materials is in full swing, single crystals are still on the top in vital areas like radiation detection (γ-ray, X-ray, neutron, IR), solid state lasers, optical windows etc., and even in nano technologies like thin films and quantum dots, the substrates used are invariably made from single crystals.

The effective NLO single crystals with efficient optical frequency conversion are the key elements for the development of laser systems, telecommunication, optical information processing, high optical disk data storage, wide range tunable sources of coherent illumination in ultra-violet, visible and infrared spectral ranges. Hence, there is a great demand to synthesize new NLO materials and grow their single crystals.

Amino acids are interesting materials for NLO applications as they have proton donor carboxyl acid groups (COO⁻) and proton acceptor amino groups (NH₂⁺). In recent years, efforts have been made on amino acid with organic and inorganic complexes for potential nonlinear optical (NLO) applications. Semiorganic materials possess several attractive properties such
as high NLO coefficient, high laser damage threshold and wide transparency range, high mechanical strength and thermal stability, which make the materials suitable for second harmonic generation (SHG) and other NLO applications. Complexes of amino acid with inorganic salts are promising materials for optical SHG, as they have a tendency to combine the advantage of the organic amino acid with that of the inorganic salt.

The present study on effective semiorganic NLO materials reveals that amino acid based L-valine zinc hydrochloride, L-valinethiourea hydrochloride, L-valine l-valinium orthophosphate and L-valine l-valinium nitrate single crystals are valuable and applicable materials for potential applications in high power lasers. Oxalic acid based Potassium hydrogen oxalate and Magnesium sulphate doped Potassium borooxalate were also synthesized and identified as NLO materials. More thrust has been emphasized on the second harmonic generation properties of the grown crystals.

These grown crystals were subjected to characterization techniques such as single crystal X-ray diffraction, CHNS (Carbon, hydrogen, nitrogen and sulphur) analysis, EDAX (Energy dispersive X-ray analysis), FTIR (Fourier transform infrared spectroscopy), UV-VIS-NIR spectroscopy, Vickers microhardness, DTA-TGA (Differential thermal analysis and Thermogravimetric analysis), DSC (Differential scanning calorimetry), Dielectric studies, laser damage threshold, second harmonic generation (SHG), a.c. impedance spectroscopy, and photoconductivity studies to assess their structural, thermal, mechanical, electrical, linear and nonlinear optical properties.

**Chapter One** gives an elaborate introduction to crystals. The various methods of crystal growth are explained in this chapter, with an emphasis to solution growth technique. The theoretical concept of nonlinear
optics has been explained thoroughly. The objectives and the scope of the thesis have been presented in this chapter.

Chapter Two deals with the review on literature survey of nonlinear optical crystals built from organic, inorganic and semiorganic materials. An overview of the various principles and instrumentation techniques, which are used to characterize the grown crystals are also presented in this chapter. The principle, theory and instrumentation involved in various characterization techniques such as single XRD, CHN analysis, FT-IR, UV-Vis-NIR spectra, thermal, hardness, dielectric, A.C. impedance spectroscopy, SHG efficiency, laser damage threshold, and photoconductivity studies are presented in detail in this chapter.

Chapter Three deals with the growth and characterization of L-valine zinc hydrochloride (LVZHCl) and L-valinethiourea hydrochloride (LVTHCl) semiorganic nonlinear optical single crystals.

The semiorganic single crystals of L-valine zinc hydrochloride (LVZHCl) and L-valinethiourea hydrochloride (LVTHCl) were grown using water as solvent from slow evaporation solution growth technique (SEST) at room temperature. The crystals belong to monoclinic system. The lattice parameters of the crystals were indexed from single crystal X-ray diffraction analysis. The FTIR spectral analysis was carried out to identify the chemical bonding and molecular structure of the crystals. The vibrational analysis showed the presence of NH$_3^+$ ion confirming the protonation of amino group leading to the formation of L-valine zinc hydrochloride and L-valinethiourea hydrochloride. The CHNS analysis was carried out on the grown crystals to estimate percent composition of the elements in the sample and the stoichiometric ratio of the compounds were verified. The optical properties of the crystals were determined using UV-
visible spectroscopy. From the optical spectrum it was found that the cut-off wavelength for LVZHCl and LVTHCl was around 213 nm and 257 nm respectively, and the maximum transmission are in the wavelength range 260-1100 nm, which are most desirable characteristics of a NLO material for applications. The optical band gap of LVZHCl and LVTHCl was calculated as 5.83 eV and 4.83 eV respectively. Kurtz and Perry powder technique was employed to test the second harmonic generation effect in the grown crystals, which was confirmed by the emission of green light.

From the TGA/DTA analysis, it was found that the melting point of LVZHCl and LVTHCl is around 277.3°C and 312.7°C respectively. The dielectric studies reveal the low dielectric constant and low dielectric loss of the crystals at high frequency range, which is ideal for NLO materials. The laser damage threshold value of LVZHCl and LVTHCl was calculated as 0.75 GW/cm² and 0.95 GW/cm². The mechanical stability of the crystals was assessed by Vickers microhardness test. The values of Meyers’ index suggest that both the crystals belong to soft category.

The photoconductivity analysis was carried on both the crystals to study the variation of dark and photocurrent with the applied electric field and it was found that both the crystals possess negative photoconductivity. The crystals were also studied using a.c. impedance spectroscopy to explore their piezoelectric properties. All these studies indicate that LVZHCl and LVTHCl crystals can be considered as potential candidates for the fabrication of optoelectronic devices.

**Chapter Four** gives a detailed account of the studies conducted on the characterization of single crystals of the charge transfer complexes of L-valine l-valinium orthophosphate (LVP) and L-valine l-valinium nitrate (LVN) grown by slow evaporation solution growth technique at ambient temperature. The structure of LVN was solved by the direct method and
refined by the full matrix least-square technique using the SHELXL-97 program.

The organic-inorganic complexes of L-valine l-valinium orthophosphate (LVP) and L-valine l-valinium nitrate (LVN) were synthesized and grown by slow evaporation solution growth technique at room temperature using double distilled water as the solvent. Himedia L-valine and Merck GR grades of Orthophosphoric and Nitric acids were selected to maintain the purity of the precursors. LVP crystal crystallized under orthorhombic system with \( P2_12_12_1 \) space group. The LVN crystals crystallized under monoclinic system with \( P2_1 \) space group. The noncentrosymmetric structures of the crystals were confirmed from the assigned space groups.

The X-ray diffraction intensity data for LVN single crystals were measured at 296(2) K on a Bruker kappa apex2 CCD diffractometer with a graphite monochromatic \( \text{Mo}_K\alpha \) radiation, \( \lambda = 0.71073 \text{ Å} \). The \( \omega:2\theta \) scan technique was employed to measure 2218 reflections up to \( \theta = 27.96^\circ \) and 2052 reflections were unique. The crystal structure was solved by direct methods and refined by a full-matrix least squares procedure based on \( F(000) \). A single weighting scheme was applied and the refinement continued until the final deviation factors \( R \) and \( R_w \) were 0.0406 and 0.1203, respectively.

The nature of co-ordination and the functional groups present were investigated by the Fourier transform infrared spectrum. The vibrational analysis revealed the zwitterionic nature of the crystals. The optical behavior was analyzed using UV-Vis-NIR studies. The UV cut-off wavelength of LVP and LVN was recorded as 228 nm and 260 nm. The optical bandgap energy of LVP and LVN was found to be 5.45 eV and 5.62 eV respectively. The wide energy band gap shows that the defect concentration in the grown crystals is very low and large transmittance in the visible region. Both the crystals
showed positive second harmonic generation verified by classical Kurtz and Perry powder technique.

The thermal stability of the crystals was measured with the help of TGA/DTA analysis. As the crystals decompose around the melting temperature, the melting technique cannot be used to grow the amino acid crystals. The molecular composition and empirical formula of LVP and LVN were confirmed by CHNS analyzer. Vickers microhardness analysis carried out on the materials suggests that the crystals belong to the soft category. The crystals were further subjected to A.C. impedance analysis and the specific resonant behavior of the crystals electrical impedance was observed under the influence of the external electric field. The photoconductivity studies of the crystals revealed the negative conductivity nature of the crystals. The dielectric profiles of the crystals studied at room temperature indicated that the capacitance, dielectric constant and dielectric loss decreased with increase in frequency which is the normal behavior of nonlinear optical materials. Owing to these properties LVP and LVN could be promising materials for the nonlinear optical applications involving frequency-doubling processes.

Chapter Five includes the details of the growth and characterization techniques to assess the nonlinear optical properties of Potassium hydrogen oxalate (KHO).

The semiorganic nonlinear optical material Potassium hydrogen oxalate (KHO) was grown by slow evaporation solution growth technique at room temperature using double distilled water as the solvent. Merck GR grades of Potassium hydroxide pellets and Oxalic acid dihydrate were taken as the precursors in the equimolar ratio. The calculated amount of the reactants was taken in the equimolar ratio and stirred using magnetic stirrer to obtain a homogenous concentration. The anhydrous product was a white, odorless, crystalline solid, hygroscopic and soluble in water (2.5 g/100 g at room
temperature). The nonlinear optical nature of the crystal was confirmed by single crystal XRD analysis and Kurtz-Perry powder technique. The crystal crystallized under monoclinic system with a noncentrosymmetric space group P2$_1$/c. The stoichiometric ratio of the elements in KHO was confirmed by CHNS analyzer. The coordination of Potassium hydroxide with Oxalic acid dihydrate was confirmed by FTIR studies. The UV spectra shows the presence of a wide transparency window lying between 200 nm and 1100 nm with $\lambda_{\text{max}}=221$ nm. The forbidden energy gap was estimated from the relation $E_g=1.243\times10^3/\lambda_{\text{max}}$ and is found to be of 5.62 eV which is typical of dielectric materials. The wide energy band gap shows that the defect concentration in the grown crystals is very low and large transmittance in the visible region.

Thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) are of immense importance as far as the fabrication technology is concerned as they serve indicators for thermal stability of the material for fabrication where by a considerable amount of heat is generated during the cutting process. TGA and DTA for KHO were recorded using a simultaneous thermal analyzer. The DTA graph shows one sharp endothermic peak at 211.4°C, which corresponds to the melting point of the sample. The TG curve gives the detailed decomposition of the material. The compound undergoes endothermic decomposition that results in 74.4% weight loss between 200°C and 300°C. The weight loss is due to release of gaseous products like CO$_2$, CO and water molecules. The residue left after 60.0°C is Potassium oxide which is about 25.18%.

Vickers microhardness values have been calculated using $H_v=1.8544P/d^2$ kg/mm$^2$, where ‘P’ is the applied load in kg and ‘d’ is the mean diagonal length of the indenter impression. The higher hardness value also confirms the excellent chemical stability of KHO at room temperature. The Meyers’ index or work hardening coefficient was calculated as 4.99,
suggesting the soft nature of the crystal. The dielectric constant and dielectric loss of the crystal were studied as a function of frequency at room temperature. The behavior of low dielectric loss with high frequency for the sample suggests that the crystal possesses enhanced optical quality with lesser defects and this parameter plays a vital role for the fabrication of nonlinear optical devices. Laser damage threshold studies have been carried out for the solution grown KHO single crystals using a Q-switched Nd: YAG laser of pulse width 6 ns at a wavelength of 1064 nm and a 10 Hz repetition rate operating in TEM$_{00}$ mode, used as a source. In the present study it was found to be 5.8 GW/cm$^2$.

Chapter Six discusses the effect of doping Magnesium sulphate in potassium borooxalate.

The semiorganic nonlinear optical (NLO) 1 mole % Magnesium sulphate doped in Potassium Borooxalate (1 mole % MgSO$_4$ doped inKBO) single crystals have been grown by Slow Evaporation technique at ambient temperature. Merck GR grade, Magnesium sulphate heptahydrate, Potassium hydroxide, Boric acid and Oxalic acid along with de-ionized water were used for the synthesis and growth. The crystal belongs to the orthorhombic system with a noncentrosymmetric space group P2$_1$2$_1$2$_1$.

The presence of Magnesium, Potassium in the crystal was identified by EDAX measurements. In order to analyze the presence of functional groups qualitatively in the grown crystal, the FTIR spectrum was recorded between 400 cm$^{-1}$ and 4000 cm$^{-1}$. The vibrational assignments confirm the presence of potassium and borate ions in the crystal lattice of oxalic acid. The optical absorption and transmittance spectrum gives information about the structure of the molecule because the absorption of UV and Visible light involves promotion of the electron in the $\sigma$ and $\pi$ orbital from the ground state to higher states. The crystal has excellent transmission in the entire visible region. The
lower cut off wavelength is 240 nm. The forbidden gap energy gap (E_g) of 1 mole % MgSO4 doped in KBO was estimated to be 5.17 eV, which is typical of dielectric materials.

The thermogravimetric analysis (TG) and differential thermo-gravimetric analysis (DTA) of the crystals were carried out for the sample weight of 22.620 mg between 50 °C and 1000 °C at a heating rate of 20 K/min in nitrogen atmosphere and the crystal is thermally stable up to 196 °C. The selected smooth surfaces of the crystal were subjected to indentation tests. For each load several trials of indentations were carried out. The Vickers microhardness analysis suggested moderate mechanical stability of the crystals. By Meyers’ law, the value of Meyers’ index ‘n’ estimated to be 2.5, indicated that the crystal belonged to soft material category. The SHG efficiency of the crystal was found to be 1.5 times that of Potassium dihydrogen phosphate (KDP).

Chapter Seven gives a summary of the important outcomes of the present investigations. It also gives a comparative assessment on the prospects of the six single crystals investigated in the present work and is listed in Table 7.1.
<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Properties</th>
<th>LVZHCl</th>
<th>LVTHCl</th>
<th>LVP</th>
<th>LVN</th>
<th>KHO</th>
<th>1 mole % MgSO₄ doped in KBO</th>
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</thead>
<tbody>
<tr>
<td>2</td>
<td>Single XRD (Å)</td>
<td>a=9.581 b=5.250 c=11.999 α=90° β=91.18° γ=90°</td>
<td>a=9.661 b=5.253 c=12.057 α=90° β=90.69° γ=90°</td>
<td>a=5.286 b=9.75 c=11.98 α=90° β=90° γ=90°</td>
<td>a=9.670 b=5.249 c=12.064 α=90° β=90.81° γ=90°</td>
<td>a=4.295 b=12.819 c=7.629 α=90° β=90° γ=90°</td>
<td>a=3.74 b=9.50 c=17.77 α=90° β=90° γ=90°</td>
</tr>
<tr>
<td>3</td>
<td>Crystal system</td>
<td>Mono clinic</td>
<td>Mono clinic</td>
<td>Ortho rhombic</td>
<td>Mono clinic</td>
<td>Mono clinic</td>
<td>Ortho rhombic</td>
</tr>
<tr>
<td>4</td>
<td>Space group</td>
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<td>P2₁/2₁2₁</td>
<td>P2₁</td>
<td>P2₁/c</td>
<td>P2₁2₁2₁</td>
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<td>5</td>
<td>UV cut-off wavelength nm</td>
<td>213</td>
<td>257</td>
<td>228</td>
<td>260</td>
<td>221</td>
<td>240</td>
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<tr>
<td>7</td>
<td>E₉ eV</td>
<td>5.83</td>
<td>4.83</td>
<td>5.45</td>
<td>4.78</td>
<td>5.62</td>
<td>5.17</td>
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<td>8</td>
<td>Melting point °C</td>
<td>277.3</td>
<td>312.7</td>
<td>260.3</td>
<td>194.7</td>
<td>211.4</td>
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<tr>
<td>9</td>
<td>Meyers’ index</td>
<td>6.66</td>
<td>4.35</td>
<td>5.39</td>
<td>6.29</td>
<td>4.99</td>
<td>2.5</td>
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<tr>
<td>10</td>
<td>Nature of crystal</td>
<td>Soft</td>
<td>Soft</td>
<td>Soft</td>
<td>Soft</td>
<td>Soft</td>
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<tr>
<td>11</td>
<td>Nature of photoconductivity</td>
<td>Negative</td>
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<td>Negative</td>
<td>Negative</td>
<td>Positive</td>
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<td>12</td>
<td>Laser damage threshold GW/cm²</td>
<td>0.75</td>
<td>0.95</td>
<td>0.85</td>
<td>0.65</td>
<td>5.8</td>
<td>10.8</td>
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<tr>
<td>13</td>
<td>SHG w.r.t. KDP (Scaling factor = 1)</td>
<td>0.95</td>
<td>0.95</td>
<td>0.603</td>
<td>0.647</td>
<td>0.772</td>
<td>1.5</td>
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</table>
7.2 SUGGESTIONS FOR FUTURE WORK

The results of the present investigations allow ample scope for further investigations in these single crystals as outlined below:

- Z-scan studies can be employed to analyze higher order harmonics.
- Analysis of Surface quality and defect mechanisms by Scanning electron microscope (SEM) and Atomic force microscope (AFM).
- Origin of laser damage mechanism and its pattern can be studied in much detail.
- Investigate the nucleation parameters such as metastable zone width, induction period, interfacial tension etc., to improve and investigate the optimized growth parameters.
- Systematic study of pH of solution will throw more light on the morphology and the growth rate of the crystals.
- Effect of deuteration on the linear and non-linear optical properties of the crystals to enhance the SHG efficiency.
- Attempts could be made to grow large size crystals by other crystal growth techniques for possible industrial utility.
- Attempts could be made to improve SHG efficiency by incorporating rare earth metal ions (La, Ce, Yb, and Tb) for frequency conversion devices.
- Frequency doubling is a phase-sensitive process which usually requires phase matching to be efficient and hence the phase matching study for the crystals is to be done. The optimum crystal length and pump beam radius, taking into account factors such as beam divergence, spatial walk-off, group velocity mismatch, beam quality etc are to be studied in detail for device fabrication applications.
- Synthesis of the crystals in nanocrystalline form, possibly by sol gel or CVD techniques.