CHAPTER 7

SUMMARY AND SUGGESTION FOR FUTURE WORK

This thesis deals with the growth and characterization of five crystals, viz. L-lysine monohydrochloride dihydrate (L-LMHCl dihydrate), strontium bis (hydrogen l-malate) hexahydrate (SrLM), sodium di(l-Malate) borate (NaDMB), sodium acid phthalate (NaAP) and lithium hydrogen phthalate dihydrate (LHP). Two growth methods (low temperature conventional solution growth method and unidirectional SR method) are adopted to grow single crystals. Various physical properties of these crystals are studied both from fundamental and application points of view. This chapter summarizes the main results obtained in this work and the suggestion for future work is discussed at the end.

7.1 SUMMARY

Nonlinear-optical phenomena are put to practical use with the help of laser beams and non-linear optical crystals are playing a prominent role in several critical technologies. Whether it is as SHG, THG and Pockels cells in a field like inertial confinement fusion, or higher harmonic generation of Nd:YAG laser in fields like material processing, semiconductor lithography, laser micromachining, laser spectroscopy and photochemical synthesis, a variety of nonlinear optical crystals are in high demand. Optical-quality single crystals are critically important for these nonlinear and electro-optic applications.
Crystal growth, which was earlier a relatively narrow field of materials science, has now been identified as a thrust area among the major areas of science and technology. This became true after the discovery of novel materials which bridge the gap between technology and human life. Growth of single crystals is one of the standard and important techniques in the optical industry involving the production of large crystals.

Solution growth is one of the earlier and universal techniques used by several researchers in establishing the crystal growth process. The aqueous solution growth is a simple process, but yields bulk crystals with fewer defects useful for device applications. As the growth proceeds close to the room temperature, this technique results in high quality for device applications. Materials having moderate to high solubility can be grown by low temperature solution growth method. Several industrially and technologically important materials are grown by low temperature solution growth. The growth of crystals from low temperature solutions occupies a prominent place especially when materials are not stable at elevated temperatures. This technique is useful in providing constraint-free single crystals, and identification of suitable solvent is the primary step in this procedure. A saturated solution containing a solute exceeding the equilibrium value on the solubility curve with meta-stable domains is used. In particular, slow cooling of saturated solution, solvent evaporation, and temperature difference between regions of growth and dissolution processes have been used to grow single crystals from solutions.

Large unidirectional bulk single crystals are usually essential for device fabrication, and it must be possible to grow crystals of good optical quality for utilization. Recently invented SR method is effective method to grow unidirectional good quality crystals by low temperature solution growth. Single crystals of L-lysine monohydrochloride dihydrate (L-LMHCl
dihydrate), strontium bis (hydrogen l-malate) hexahydrate (SrLM), sodium di(l-Malate) borate (NaDMB) and sodium acid phthalate (NaAP) by low temperature conventional solution growth method and unidirectional SR method were grown. Single crystals of Lithium hydrogen phthalate dihydrate were grown by conventional solution growth method.

Unidirectional growth of largest L-Lysine mono hydrochloride dihydrate (L-LMHCl) crystal, a semiorganic nonlinear optical material, was grown from SR method. The solubility and metastable zone-width of L-LMHCl dihydrate was estimated using Millipore water (18.2 MΩ cm). L-LMHCl dihydrate has a positive gradient of solubility. In the case of L-LMHCl dihydrate, the metastable zone width first decreases and then increases with increasing temperature. Due to high solubility the L-LMHCl dihydrate solution is more viscous at higher temperature. For higher viscous solution, there is an increase in zone width, since the viscosity of the solution greatly reduces the motion of solute molecules in the solution thus providing barrier for nucleation. The gravity driven concentration gradient effect was investigated in the SR crystallizer. The 30, 60 and 90 cm ampoules were used for this study. The L-LMHCl dihydrate crystals were growing initially at the rate of 1.5, 2.5 and 3 mm/day, respectively, for 30, 60 and 90 cm ampoules. This is due to gravity driven concentration increase at the bottom of the ampoule, the longer column resulting in higher concentration.

The growth rate of L-LMHCl dihydrate crystal along the <0-11>, <01-1>, <011> and <100> orientations was investigated by the SR method. The L-LMHCl dihydrate crystals were growing at the rate of 1 mm/day in the orientations <0-11>, <01-1>, <011>. The <100> orientation crystal was growing at the rate of 2 mm/day. The faces which have higher attachment energy grow faster. The <100> orientation face has more attachment energy than the other orientations. The experimental setup of the SR method has been
modified in some aspects and L-LMHCl dihydrate crystals were grown. The fast growth orientation <100> was used for growth of large size L-LMHCl dihydrate crystals. Bulk size cylindrical shape 70 mm length 80 mm diameter good quality L-LMHCl dihydrate crystal was grown after 30 days with an average growth rate of 2.5 mm/day. The transparency of the crystal was measured from 200 to 1100 nm using the UV-Visible - NIR spectrometer. At 225 nm a sharp fall of transmittance was observed, indicating a single transition in near UV region of L-LMHCL dihydrate. It has a good transparency (80%). High resolution X-ray diffraction (HRXRD) and birefringence studies show that the SR method crystal quality was good. The dielectric constant of the sample was measured for the applied frequency that varies from 20 Hz to 1 MHz at different temperatures (40 to 60 °C). The dielectric constant and dielectric loss have high values in the lower frequency region and then it decreases with the applied frequency. The piezoelectric coefficient $d_{33}$ value was measured at constant frequency which shows that L-LMHCl dihydrate crystal exhibits piezoelectric nature.

Growth of good quality bulk single crystal of strontium bis (hydrogen l-malate) hexahydrate (SrLM) was difficult in slow evaporation solution growth Technique (SEST). The slow cooling and unidirectional growth by SR method were preferred. SrLM was synthesized from the starting materials namely, L-malic acid and strontium hydroxide (octa hydrate). L-malic acid and strontium hydroxide (octa hydrate) were dissolved in Millipore water (18.2 MΩ cm) in mole ratio 2:1. The prepared mixture was stirred well for six hours by using a motorized magnetic stirrer at 60 °C. The solution was maintained at 36 °C and kept in a constant temperature bath. After 8 days the SrLM material was crystallized at the bottom of the container. The synthesized polycrystalline SrLM material was analyzed using powder XRD.
The solubility and metastable zone-width of SrLM was estimated for Millipore water. SrLM has a positive gradient of solubility. The metastable zone width decreases with increasing temperature. The growths of SrLM single crystals were carried out by low temperature solution growth technique by cooling and unidirectional solution growth by SR method. Transparent and good quality seeds (5 mm × 2 mm × 2mm) obtained from slow evaporation solution technique were selected for the growth of both the methods. A constant temperature bath controlled to an accuracy of ± 0.01 °C was used for the Low temperature solution growth technique by cooling.

Optically transparent, SrLM single crystal of size 24 mm × 5 mm × 6 mm with well defined morphology was grown by slow cooling technique. Based on the morphology of the conventional SEST grown SrLM crystal, the (010) plane was selected in SR method to impose the orientation in the growing crystal. The seed crystal was carefully placed at the bottom of 1 ft length and 10 mm diameter ampoule. We found that the seed crystal started to grow after 12 days. The very high quality crystal of 50 mm length and 10 mm diameter was grown in a period of 34 days.

The X-ray diffraction data reveals that the crystal belongs to the orthorhombic system with space group P2₁P2₁P2₁. The various functional groups present in the grown material have been identified using FTIR spectra. The transparency of the crystal was measured from 200 to 1100 nm using the UV-Visible spectrometer. The SrLM crystal was quite transparent and the cutoff wavelength was 226 nm. The transmittance of SR method grown SrLM crystal (59 %) is 12 % higher than the transmittance of the slow cooling method grown SrLM crystal (47 %). The birefringence studies show that SR grown crystal was better in quality than conventional method grown crystals. The dielectric constant of the sample was measured for the applied frequency that varies from 100 Hz to 1 MHz at different temperatures (45 to 60 °C). The observations were made while cooling the sample. The dielectric constant and
dielectric loss have high values in the lower frequency region and then it decreases with the applied frequency.

The dielectric constant in SR method grown crystal is higher than conventional method grown crystal. The dielectric loss was less in SR method grown crystal as against conventional method grown crystal. Thermal properties of the material were studied by Thermogravimetric, differential thermal analyses (DTA) and melting point apparatus. It is seen from the curves that the melting point of the material is around 76 °C which was also confirmed by Monatch melting point apparatus. The SrLM Material was stable up to 60 °C. The second-harmonic generation efficiency was estimated by Kurtz and Perry powder technique. The SHG relative efficiency of SrLM crystal was found to be 3.4 times that of KDP. Vickers microhardness was calculated in order to understand the mechanical stability of SrLM crystals. It is seen that the hardness of (010) plane increases with the increase of load. Crack initiation and materials chipping become significant beyond 100 g of the applied load so hardness test cannot be carried out above this load. The hardness for SR grown crystal is very much higher than the hardness of conventional method grown crystal.

Sodium di (L-malato) borate (NaDMB) was synthesized from the starting materials namely, L-malic acid, sodium hydroxide and boric acid. L-malic acid, sodium hydroxide and boric acid were dissolved in Millipore water in mole ratio 2:1:1. The prepared mixture was stirred well for six hours by using a motorized magnetic stirrer at 50 °C and clear solution was obtained. The solution was taken in a covered container for controlled evaporation and kept in a constant temperature bath at 40 °C. After 15 days the NaDMB material was crystallized at the bottom of the container. The solubility and metastable zone width of NaDMB was estimated for water solvent. NaDMB has a positive gradient of solubility. The metastable zone width decreases with increasing temperature.
The growths of NaDMB single crystals were carried out by low temperature solution growth technique by slow evaporation and unidirectional solution growth by SR method. Optically good quality bulk single crystal of NaDMB (22 mm × 8 mm × 6 mm) was successfully grown by slow evaporation solution technique. Based on the morphology of the conventional SEST grown NaDMB crystal, the (010) plane was selected in SR method to impose the orientation in the growing crystal. Optically transparent good quality crystal of 47 mm length was grown in a period of 32 days. The grown crystals were subjected to single crystal and powder X-ray diffraction studies to identify the morphology and for confirming that the crystal belongs to monoclinic structure with space group P21. FTIR spectra reveal the functional group identification. The UV-Vis - NIR spectrum elucidates that the crystal is transparent between 245- 1100 nm and the lower cutoff is found to be around 240 nm. The rocking curve measurements substantiate the good quality of the crystals. SR method grown crystal has greater crystalline perfection than conventional method grown crystal as the FWHM is much lesser for the former one.

The thermogravimetric (TG) and differential thermal analysis (DTA) traces reveal the thermal stability of the sample. TG/DTA studies reveal that the crystal was thermally stable up to 272 °C. Microhardness studies have been carried out to assess the mechanical properties. It is seen that the hardness value for SR method grown crystal is higher than the hardness of SEST grown crystal. The nonlinear optical (NLO) property of the crystal has been confirmed by Kurtz powder technique and second harmonic generation efficiency was found to be 1.2 times that of potassium dihydrogen orthophosphate (KDP) crystal.

Initially sodium acid phthalate (NaAP) was synthesized by dissolving stoichiometric amounts of sodium bicarbonate and phthalic acid in
Millipore water. The transparent rhombic crystals form as the major product on evaporation at room temperature. The synthesized polycrystalline NaAP material was analyzed using powder XRD. It was observed from the single crystal X-ray diffraction analysis that the crystal belongs to orthorhombic crystal system having non-centro symmetry with B2ab space group. The solubility and metastable zone-width of NaAP was estimated for Millipore water. NaAP has a positive gradient of solubility. The metastable zone width decreases with increasing temperature. The growth was carried out by a unidirectional Sankaranarayanan-Ramasamy (SR) method. The optically transparent NaAP crystal was grown by conventional SEST and a well faceted crystal was chosen as a seed for SR Method. Based on the morphology of the conventional SEST grown NaAP crystal, the (001) plane was selected in the present study to impose the orientation in the growing crystal. The seed crystal started to grow after 12 days. The very high quality crystal of 36 mm length and 20 mm diameter has grown in a period of 35 days.

The NaAP crystal was cleaving perpendicular to the <001> direction. The <001> directional grown NaAP crystal was easily cleaved as a thin wafer of size 0.5 mm without any damage. The cleaved wafer, fabricated out of the SR grown NaAP single crystal was subjected to X-ray diffraction analysis. It shows a single sharp peak. The recorded spectrum confirms the unidirectional growth. High resolution X-ray diffraction (HRXRD) study shows that SR method grown crystal has greater crystalline perfection than conventional method grown crystal as the FWHM is much lesser for the former one. The transmittance behaviour of NaAP has been analysed. It is observed that the crystal has good transmission in the entire visible and IR region and the lower cutoff of the NaAP is at 320 nm. The transmittance of SR method grown NaAP crystal is 3 % higher than the transmittance of the SEST - grown NaAP crystal. The birefringence calculated along the <001>
axis of the crystal is 0.0146030. The birefringence interferogram shows good refractive index homogeneity of the NaAP crystal. Optical damage tolerance of SR grown NaAP crystal was investigated by laser damage threshold studies. The NaAP crystals grown by SR method and SEST were subjected to Vickers micro hardness testing. The micro hardness value of <001> NaAP crystal was found to be initially increasing with increase of load and then slowly decreases with further increase of load. The cracks are formed around 100 g for SR grown crystals and around 50 g for SEST grown crystals.

Initially LHP dihydrate was synthesized by dissolving high-purity lithium hydroxide and phthalic acid in millipore water in mole ratio of 1:1. The product was purified by repeated recrystallization before it was used for solubility studies and growth of LHP dihydrate crystals. The solubility of LHP dihydrate was determined for six different temperatures namely 35, 40, 45, 50, 55 and 60 °C. LHP dihydrate has a positive gradient of solubility. Slow evaporation technique is employed to grow the single crystals of LHP dihydrate in aqueous solution. After 25 days, optically transparent good quality crystals were harvested with a maximum size of 10 mm × 10 mm × 5 mm. The synthesized polycrystalline LHP dihydrate material was analyzed using powder XRD.

It was observed from the single crystal X-ray diffraction analysis that the crystal belongs to orthorhombic crystal system with pnma space group. The structural perfection of the grown crystal has been analyzed by high resolution X-ray diffraction (HRXRD) rocking curve measurements. The full width at half maximum (FWHM) of the diffraction curves is 11 arc s, which is very close to that expected for a nearly perfect crystal and showing that the crystalline perfection is excellent. Vibrational frequencies were assigned from FTIR spectral analysis, which confirm the presence of functional groups of the LHP dihydrate. The transmittance behaviour of LHP
dihydrate has been analysed. It is observed that the crystal has good transmission in the entire visible and IR region and the lower cutoff of the LHP dihydrate is around 330 nm. The dielectric constant and dielectric loss studies of LHP dihydrate establish the normal behaviour. The fluorescence studies indicate that LHP dihydrate crystals have a blue fluorescence emission. The TG weight losses were used to formulate a fitting decomposition pattern for the compound. The DTA thermogram conforms to the TG weight loss pattern. The microhardness study was performed on LHP dihydrate crystal, which shows an increase in hardness value with increase in load.

### 7.2 SUGGESTION FOR FUTURE WORK

The metastable zone width can be increased by the addition of some complexing salts like potassium chloride (KCl), ethylenediamine tetraacetic acid (EDTA), sulfosalicylic acid in solution. Fast growth using SR technique with enhanced metastable zone width may be effective in growing bulk crystals. Growth of single crystals of substances that have negative coefficient of solubility can also be tried by SR method.

SrLM and NaDMB are promising NLO materials to explore. SrLM and NaDMB exhibit second harmonic efficiencies 3.4 and 1.2 times that of KDP. Hence, various NLO related studies may be carried out. Experiments may be performed to determine the nonlinear optical, electro-optic, piezoelectric and nonlinear absorption coefficients which are important parameters for NLO element. L-malic acid derivatives are potential candidates for NLO and electro-optic applications. Efforts can be made to grow L-malic acid derivative crystals by SR-method and their properties can be investigated.
NaAP is extensively studied in terms of its growth, optical, perfection and hardness properties. Doping of crystals is known to change their physical and chemical properties. This aspect has not been dealt with so far in NaAP. Also, the electro-optic and piezoelectric effects in SR grown crystals are not yet studied and hence may be taken up for further studies. Doped sodium acid phthalate (NaAP) crystals can be grown by the conventional solution growth method and SR method. The impurities chosen can be inorganic, organic and semiorganic NLO materials. Since NaAP is a semiorganic material having the combined nature of organic and inorganic material, the impurities of both class are expected to have significant influence. Hence impurities like potassium dihydrogen ortho phosphate (KDP), urea and L-arginine phosphate (LAP) can be chosen as dopants. Effect of these inpurities on the growth kinetics, surface and habit morphology, structural, optical and mechanical properties can be studied. Optical and electro-optical characterisations can be carried out. Phthalic acid derivative crystals such as rubidium, thallium and cesium acid phthalates crystals can be grown by SR method. Growth of these crystals will enable the availability of wide range of substrate materials for the growth of organic and polymer NLO thin films.

Since LHP dihydrate crystal is not an SHG material, Z-scan measurements can be carried out and the third order nonlinearity can be studied. Efforts can be made to grow unidirectional bulk crystal of LHP dihydrate by SR method. Optical, mechanical and dielectric measurements can be carried out for SR grown crystal and compared with conventional solution grown crystal.

In SR method crystallization usually occurs at around room temperature; much lower thermal stress is expected in these crystals over those grown at high temperatures. This is particularly helpful for growth of
mixed crystals because thermal stresses can cause these crystals to crack easily. The mixed crystals of phthalic acid and L-malic acid derivative crystals can be grown by SR method. The influences of the composition on structure, quality, and optical properties of grown crystals can be investigated.