CHAPTER 7

SUMMARY AND CONCLUSIONS

In the present era of rapid communication system, more powerful data-systems with larger networks, faster processors and mass storage devices are required. As the need for larger digital data processing rate grows, the strength of photonics is increasingly recognized. The emergence of new materials with superior quality is often responsible for major advances in new technologies. Consequently, there have been extensive efforts to develop new kind of semi-organic nonlinear optical crystals related to amino acids, for number of applications such as second harmonic generation, frequency mixing, electro-optic modulation etc. In order to satisfy the above said requirements, the material selection is the most important factor, which depends not only on the laser conditions but also on the physical properties of the crystal, such as transparency, damage threshold, conversion efficiency, and phase matching and temperature stability. However, the development of photonic technology relies largely on the progress achieved in fabricating new optical materials with better performance. Hence, materials with nonlinear optical (NLO) response are expected to play a key role in enabling optoelectronic and photonic technologies. In order to retain the merits and overcome the short-comings of organic materials, some new classes of NLO crystals such as semi-organic crystals have been developed. At present, nonlinear optical inorganic materials are widely used for a variety of photonic technologies. With increasing demand for nonlinear applications, in the present work, attempts were made to grow potential nonlinear optical crystals needed for the upcoming photonics industry.
Single crystal of L-Alanine (LA) is a well-known organic nonlinear optical material exhibiting a low angular sensitivity and hence useful for type II second harmonic generation (SHG). In view of this, attempts have been made to synthesize and grow Pure L-Alanine, L-Alanine mixed with KCl, KBr and Maleic acid with concentrations such as 0.25, 0.50, 0.75 and 1.0. These crystals were grown with double distilled water as solvent by slow evaporation technique.

These crystals were chosen for the present study as the preliminary SHG efficiency studies, the optical, the mechanical properties and the electrical studies strongly favouring the usage of these crystals in photonics technology. Along with the growth, attempts were made to investigate structural, optical, mechanical and dielectric studies. The results of the investigations are presented and discussed.

The solubility of LA, LAPC, LAPB and LAMA crystals were determined at various temperatures. It is found to increase with temperature and at a fixed temperature it is higher for LAMA than that of LAPC and LAPB, also it is high in LAPC, LAPB and LAMA than that of L-Alanine (LA) crystal which may be attributed to the difference in ionic radii of LA, KCl, KBr and maleic acid.

Based on the solubility data, optically transparent, defect free and good quality Semi-inorganic nonlinear optical LAPC and LAPB single crystals and semi-organic nonlinear LAMA single crystals with different concentration of KCl, KBr and maleic acid respectively have been grown using slow evaporation technique from their corresponding aqueous solutions. Considerable dimensions in LA, LAPC, LAPB and LAMA single crystals have been grown in a period of 20-30 days.

The growth conditions have been optimized for all the grown crystals studied, to meet the requirements of nonlinear optical applications. The Single crystal XRD results expose that LA, LAPC, LAPB and LAMA crystals are Orthorhombic in
structure and belong to P2_12_12_1 space group. Powder X-ray diffraction patterns of LA, LAPC, LAPB and LAMA have confirmed the crystallinity and single phase nature of the crystals. As the concentration of KCl in LAPC increases, unit cell volume contracts whereas KBr in LAPB and maleic acid in LAMA increases, unit cell volume expands. This could be due to the lesser ionic radii of KCl than the KBr and maleic acid. The presence of the functional groups in the crystals of LA, LAPC, LAPB and LAMA have been identified and confirmed by FT-IR analysis.

The optical absorption spectrum of LA, LAPC, LAPB and LAMA reveals that the absorbance is less than one unit in the entire visible region. The studies indicate that LA and LAMA crystal is more transparent than that of LAPC and LAPB in the entire visible and near UV region. This transparent nature in the visible and near UV region is an essential criteria for NLO activity. The UV cutoff wavelength of LA, LAPC and LAPB and LAMA crystals decreases with increasing concentration of KCl in LAPC, KBr in LAPB and maleic acid in LAMA respectively. It reveals that the UV cutoff wavelength of all the grown crystals can be tuned by adjusting the concentration of KCl, KBr and Maleic acid in LAPC, LAPB and LAMA respectively, which makes it suitable for fabricating optoelectronic devices as per our need. Second harmonic generation efficiency of the grown LA, LAPC, LAPB and LAMA crystals were measured using Kurtz powder technique and the measured output power were compared with that of KDP. The results disclose that the materials chosen for the present investigation are phase matchable with enhanced SHG efficiency. The SHG efficiency of LAPC, LAPB and LAMA crystals are highly improved when compared with KDP crystal by a factor 2, 3 and 4 respectively. The NLO test confirmed the superiority of SHG efficiency of LAMA single crystals over LAPC and LAPB crystals, which is about 1.75, 1.28 and 2.18 times higher than that of LAPC, LAPB
and LA respectively. Hence, all the grown crystals are good candidate for frequency doubling of laser radiation.

Microhardness studies shows that the hardness number decreases with increasing load for all the grown crystals. This indicates the normal indentation size effect (ISE). Beyond 150 g load for the crystals LAPC and LAPB, significant cracks were found whereas for LAMA cracks were found beyond 75 g, which may be due to the release of internal stresses generated by indentation. The value of the work hardening coefficient was determined for all the grown crystals. It is lesser than 1.6, for LA (1.235), LAPC (1.107) and LAPB (1.057) whereas it is greater than 1.6 for LAMA (1.682) crystals. It makes clear that LA, LAPC and LAPB crystals are harder than LAMA crystals, and the LAPB crystals are the hardest of all the crystals.

The dielectric properties of all the grown crystals were studied as a function of frequency and temperature. Temperature dependent of dielectric constant ($\varepsilon_r$), dielectric loss ($\tan\delta$) and ac conductivity ($\sigma_{ac}$) has been premeditated over the temperature range of 30 to 150 °C for the frequency response of 1 kHz, 10 kHz, 100 kHz and 1 MHz. The dielectric constant and dielectric loss increases with increase in temperature and decrease with increase in frequency whereas the ac conductivity increases with increase in temperature and frequency. Interestingly, all the three parameters ($\varepsilon_r$, $\tan\delta$ and $\sigma_{ac}$) were found to depend on the composition of KCl, KBr and maleic acid in LA crystal lattices. This kind of behavior is achieved for all the thirteen crystals grown. The characteristic of low dielectric loss with high frequency for the pure LA, LAPC, LAPB and LAMA crystals suggests that they possess good optical quality with lesser defects and this parameter is of vital importance for nonlinear optical materials in their applications.
The dc conductivity measurements are carried out for the all crystals as the function of temperature range of 40 to 150 °C. It increases with increase in temperature and it is found to depend on the composition of KCl, KBr and maleic acid in LA crystal lattices, suggesting for the applications in micro electronic industry.

**FUTURE SCOPE**

In the present study slow evaporation technique was adopted for the growth experiment. Hence, attempts can be made to grow bulk size crystals by carefully adapting the slow cooling method and the chance of using high temperature can also be explored. In future, efforts can be made to identify a suitable solvent which will improve the SHG efficiency with better physicochemical properties.

Limited number of literature is available on aminoacid mixed crystals, in future other aminoacids such as L-arginine, L-asgarpic acid, L-histidine etc can be used to form the mixed crystals.

Attempts can be made to identify suitable dopants, which could provide better optical properties to boost the nonlinear optical property of these crystals.

NLO parameters such as phase matching, higher harmonic generation etc., could be estimated to make this class of materials into reality to replace the conventional materials used in laser applications. Photo conductivity and Photo-acoustic studies could be carried out on both pure and mixed crystals.

Structure and defect mechanism of the crystals can be visualized by using Atomic force microscope (AFM). By etching studies the etching behaviour of different crystallographic faces of the crystals can be examined with different organic solvents,
to identify dislocation, lattice inhomogenities and to compute crystallinity. Temperature dependent conductivity experiments can also be done in future to reckon the NLO property.