Chapter 7
SUMMARY, CONCLUSION AND FUTURE SCOPE

7.1. Introduction

In the modern era single crystals are largely used in the areas such as telecommunication, optical computing, optical data storage and optical information processing etc. Non linear optical (NLO) crystals are very important for laser frequency conversion. The NLO property of the crystal finds significant role device applications, which leads to the search for new NLO materials. As a result the research is concentrated primarily on organic compounds owing to their large nonlinearity. The NLO properties of large organic molecules and polymers have been the subject of extensive theoretical and experimental investigations during the past two decades and they have been investigated widely due to their high nonlinear optical properties, rapid response in electro-optic effect and large second or third-order hyperpolarizabilities compared to inorganic NLO materials. Inorganic materials are much more matured in their applications to second-order NLO than organics. Most commercial materials are inorganic especially for high power use. However, organic materials are perceived as being structurally more diverse and therefore are believed to have more long term promise than inorganic materials.

However the implementation of single crystals of organic materials in practical device-applications has been impeded by their inadequate transparency, poor optical quality and low laser threshold. Inorganic crystals have excellent mechanical and thermal properties, but they possess relatively modest non-linearity because of the lack of $\pi$ electron delocalization. In the recent years extensive investigations are being carried out on organo metallic and coordination complex materials, because they share the properties of
both organic and inorganic materials. Also these materials show large nonlinearity, low angular sensitivity and good mechanical hardness.

Since $\alpha$-aminoacids display specific features of interest, such as molecular chirality, which secures acentric crystallographic structures; absence of strongly conjugated bonds, leading to wide transparency ranges in the UV-Visible spectral regions; zwitterionic nature of the molecule, which favours crystal hardness. Further to that amino acids can be used as chiral auxiliaries for nitro-aromatics and other donor-acceptor molecules with large hyperpolarizabilities. Among the various methods of growing crystals, solution growth occupies a prominent place owing to its versatility and simplicity. Thus in the present study single crystals of pure and K$^+$, Na$^+$ and Zn$^{2+}$ ions doped organometallic L-Alanine Cadmium Chloride (LACC) are grown by a simple slow evaporation technique. Here the dopants are selected in such a way in comparison with the cadmium ion (Cd$^{2+}$) which is present in the pure LACC. Keeping the ionic radii of Cd$^{2+}$ ion (0.95 Å) in mind, the large ionic radii K$^+$ ion (1.38 Å), almost an equal ionic radii Na$^+$ ion (0.97 Å) and a smaller ionic radii Zn$^{2+}$ ion (0.74 Å) were chosen. In the present study the effect of the different ionic radii metal ions in the lattice of pure LACC is studied and how it alters the various properties are discussed.

7.2 Summary and Conclusion

The analytical reagents (AR) grade L-alanine, Cadmium chloride, Potassium chloride, Sodium chloride and Zinc chloride along with doubly distilled water are used for the growth of pure and K$^+$, Na$^+$ and Zn$^{2+}$ ions doped LACC crystals. The solubility of pure LACC in double distilled water was determined at 303 K. It was found to be 12.25 gram/10ml. The unit cell dimension and morphology of the pure LACC crystal was
determined using single crystal XRD data and it was found that the grown crystal belongs to the monoclinic system with space group C2 and the number of molecules per unit cell is $Z = 4$. It was again verified by powder XRD data. All the doped LACC crystals are characterized by powder X-ray diffraction. In all the cases the unitcell dimension and cell volume are calculated and they are also found to be monoclinic system. But there are slight changes in the lattice parameters of the doped LACC crystal have been noticed, it was due to the presence of impurity metal ions in the lattice of pure LACC.

The FTIR spectroscopic studies are carried out with a view of obtaining an insight into the structural aspects of pure and doped LACC crystals. The existence of functional groups and the bonding nature of pure and doped LACC crystals were understood from these studies. Since the functional groups of pure and K$^+$, Na$^+$ and Zn$^{2+}$ ions doped LACC crystals are identical, the FTIR spectra of all the grown crystals appears same. But it is observed that there is slight shifts, broadening and narrowing of absorption peaks in FTIR spectrum of K$^+$, Na$^+$ and Zn$^{2+}$ ions doped LACC crystals. This may be due to the incorporation of K$^+$, Na$^+$ and Zn$^{2+}$ ions into the lattice of LACC. Atomic absorption studies revealed the presence of K$^+$, Na$^+$ and Zn$^{2+}$ metal ions in the doped LACC crystals. In all the cases concentration of the doped metal ions increases as the doping concentration is increased. Again it was noticed that the more higher ionic radii (K$^+$) dopant ions (compared to the ionic radii of Cd$^+$ ions) have entered into to the lattice of pure LACC, next to that almost equal ionic radii (Na$^+$) dopant ions and only few number of smaller ionic radii (Zn$^{2+}$) dopant ions have entered into to the lattice of pure LACC.

The surface morphological features of all the grown crystals have been observed using a Scanning Electron Microscope (SEM). From the SEM images it was observed that
in the pure and doped LACC crystals the grain size varies from 1µm to about 3 µm. It was also noted that the alignment of grains are improved in the doped crystals when compared with pure LACC crystals. It may be due to the bunching of small grains around the impurity atom. The porosity of the K⁺ ion doped crystals increases which in turn reduces the dielectric constant of the doped crystals. On the other hand in the case of Zn²⁺ ion doped LACC crystals the porosity of the Zn²⁺ ion doped LACC crystals decreases it may be due to the smaller ionic radii Zn²⁺ ions occupy the vacancies between the lattice of pure LACC crystals. Since the porosity of the material decrease the dielectric constant increases.

An elemental analysis is carried out for all the seven crystals by employing Energy Dispersive Analysis by X-Ray (EDAX) in order to confirm the composition of elements in the pure and doped crystals. Again it was noted that as the ionic radii of the doped ion increases the mass percentage of metal ions entered in to pure LACC increases, the high ionic radii metal ion (K⁺) entered into the pure LACC is more than that of both Na⁺ and Zn²⁺ ions and the mass percentage of Na⁺ ions entered into the pure LACC is more than that of Zn²⁺ ions. This trend reveals that the higher ionic radii doped metal ions compete more with the ions present in the host material and successfully entered in to the lattice site of the host material as the ionic radii decreases this power decreases and hence the number of doped metal ions entered in to the lattice site of the host material decreases as the ionic radii of the doped metal ions decreases.

The density of the pure and K⁺, Na⁺ and Zn²⁺ ions doped LACC crystals were determined by floatation method. It was found that the density of K⁺, Na⁺ and Zn²⁺ ions doped LACC crystals were increased with increase of the concentration of dopants. The thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried
out using Perkin Elmer Thermal Analyzer. It was observed that the smaller ionic radii Zn$^{2+}$ ions doped LACC crystals are thermally more stable than that of pure LACC and potassium chloride doped LACC crystals, but less stable than that of sodium chloride doped LACC crystals. Again the thermal stability increases with increase in concentration of the dopant in all the doped LACC crystals.

The pure and doped LACC single crystals were subjected to Vickers hardness test with the applied load varying from 0.025 to 0.100 kg to understand the about mechanical property. In the present study the work hardening coefficient of all the grown crystals are greater than 1.6, and hence it was concluded that the pure and K$^+$, Na$^+$ and Zn$^{2+}$ ions doped LACC crystals belong to the category of soft material.

The UV-Vis–NIR transmittance/absorbance spectrum shows that, in all the grown crystals there were no significant absorption in the entire UV-Visible range. The lower cut at 200 nm along with good optical transparency enhances the usefulness of LACC for optoelectronic applications and it is an essential parameter for NLO applications. Again it was noticed that the optical transmittance of all the grown crystals (pure and K$^+$, Na$^+$ and Zn$^{2+}$ ions doped LACC crystals) almost same. Which indicates that the type of dopants the concentration of dopants in the present study didn’t affect or change the optical transmittance of the crystals in the entire UV-Visible region.

The powder Second Harmonic Generation (SHG) measurements for the all the grown crystals were performed using the Kurtz and Perry powder technique and hence the SHG efficiency is compared with KDP. When we dope the higher ionic radii K$^+$ ions and the almost equal ionic radii Na$^+$ ions the SHG efficiency of the material is less than that of pure LACC, but when the smaller ionic radii Zn$^{2+}$ ions are doped with pure LACC the SHG efficiency of the material is increased significantly with respect to the doping
concentration. This is due to the change in the the polarizability of the metal ions present in the material. The polarizability of the smaller ionic radii Zn$^{2+}$ ions are very much greater than that of the K$^+$ and Na$^+$ ions. Thus the SHG efficiency of the Zn$^{2+}$ ions doped LACC crystals possess high second harmonic generation efficiency and hence it can be used as an efficient frequency conversion material.

The DC conductivity measurements were carried out along the b-axis of the pure and K$^+$, Na$^+$ and Zn$^{2+}$ ions doped LACC crystals. The Zn$^{2+}$ ions doped LACC crystals have comparatively high value of DC conductivity. Also it was found that the DC electrical conductivity increases with increase in impurity concentration of metal ions. The DC and AC activation energies are calculated and found that they are varying with the addition of impurities and it takes high values in the metal ions doped LACC crystals. The dielectric constant increases with respect to increase of temperature and decreases with increase of frequency in all the seven grown crystals. In the present study it was confirmed that the presence of large ionic radii k$^+$ ion (1.38 Å) compared with Cd$^{2+}$ ion (0.95 Å) reduces the polarization power and hence reduces the dielectric constant in the k$^+$ ion doped crystals. The LACC crystals doped with Na$^+$ ions the variation of dielectric constant with temperature at different frequencies follow the same pattern of the pure LACC crystal, but with slightly higher dielectric constant values, because the ionic radii of Cd$^{2+}$ and Na$^+$ ions are almost same. In the case of Zn$^{2+}$ ion doped LACC crystals too, the variations of dielectric constant with temperature at different frequencies follow the same pattern of the pure crystal but with higher dielectric constant values. It may be due to the presence of smaller ionic radii Zn$^{2+}$ ion (0.74 Å) compared with Cd$^{2+}$ ion (0.95 Å) increases the polarization power and hence increases the dielectric constant in the Zn$^{2+}$ ion doped
crystals. Also it was noticed that the dielectric constant increases with increase of doping concentration. The nature of the dielectric loss curves of the all the grown crystals show that the dielectric loss decreases with increase of frequency and decrease of temperature. The value of dielectric loss decreases at higher frequencies. The low value of dielectric loss at higher frequencies suggests that the crystal posses enhanced optical quality with lesser defects and is of vital importance for NLO applications.

7.3 Suggestions for future work

Since the dielectric constant of the pure LACC is low it can be used as inter metal dielectric material. The microelectronic industry is searching for low dielectric constant materials. So the bulk crystals of LACC which is free from defects can be grown by slow evaporation technique or by other methods. The dielectric properties along the three principle directions can be calculated and hence it can be used for microelectronic applications. Before use it for real applications its linear as well as non-linear optical properties along the three principle axis should be studied and the actual values for the non-linear optical susceptibility tensor will need to be measured in future.

The optical properties such as refractive index, birefringence and phase matching of the pure and doped LACC crystals can be studied in future to confirm their optical utility.

Again the dielectric constant can be increased or decreased, depends on the need by doping it with smaller ionic radii metal ions or higher ionic radii metal ions, respectively. Serious attempts can be made in this regard with many other smaller as well as higher ionic radii metal ions in future.

In the present study it was found that the smaller ionic radii Zn$^{2+}$ ions significantly increased the second harmonic efficiency of the zinc chloride doped LACC crystals. This
can be extended by adding many more different doping concentration of zinc chloride with pure LACC.

Since the nucleation studies for these samples are not carried out, attempts can be made in future to investigate the nucleation parameters such as metastable zone width, induction period, interfacial tension etc., to improve and investigate the optimized growth parameters for industrial crystallization. In future, attempts can be made to improve the quality of the grown crystals; etching studies can be made on different crystallographic faces of the crystals with suitable etchants in order to identify the dislocations.

Since research on amino acid based organo metallic crystals are very much significant in these days, attempts can be made in future to synthesize the amino acid based LACC crystals with suitable impurities which are useful for several biomedical applications.