2. SIGNIFICANCE OF METAL SULPHATES AND AMINOACIDS SINGLE CRYSTALS

2.1. Metal sulphate single crystals

Crystallization of heptahydrate sulphate with the general formula RSO₄.7H₂O (R= Mg, Zn, Ni) material has become an important field of research for both academic interest and industrial applications in various areas like medical, agricultural and chemical industry [41-42]. MgSO₄.7H₂O, epsomite, as a source of Mg²⁺ ions has wide application in medical (like acute management of cardiac arrhythmia, migraine attacks, spasms in cerebral blood vessels) and agricultural industry (as fertilizer) [42]. The crystal structure of MgSO₄.7H₂O is orthorhombic. The pure epsomite crystals were grown at low temperature from aqueous solutions [44-49]. Zinc vitriol (ZnSO₄.7H₂O) possesses wide range of applications in the field of telecommunication, solar systems for solar energy storage, coagulation bath for rayon and optical information storage devices. ZnSO₄.7H₂O belongs to a family of inorganic non linear optical crystal [50,51,55]. Zinc vitriol is used to supply zinc in fertilizers, making lithopone, electrolyte for zinc plating, dyeing as a mordant, and also used as a preservative for skins, leather, an astringent in medicine and emetic. ZnSO₄.7H₂O crystallizes in the orthorhombic form. Nickel sulphate heptahydrate, NiSO₄.7H₂O crystal is orthorhombic with a tetra molecular unit cell of dimensions [52], a = 11.86Å, b = 12.08 Å and c = 6.81Å and is isomorphous with MgSO₄.7H₂O and ZnSO₄.7H₂O.
2.1.1 General properties and their importance

Magnesium sulphate heptahydrate (MSH) known as epsomite, MgSO$_4$.7H$_2$O, is a hydrogen bonded crystal belonging to the orthorhombic crystal system with a tetramolecular unit cell of dimensions $a = 11.86$ Å, $b = 11.99$ Å and $c = 6.85$ Å [52]. It is an example of hydrogen bonded system and isomorphous with NiSO$_4$.7H$_2$O and ZnSO$_4$.7H$_2$O. The structure of epsomite projected along [100] direction is shown in the figure 2.1. The molecular weight and density are 246.48 and 1.68 g/cm$^3$, respectively. The crystal is colourless and transparent in nature. The solubility at 30°C is $\approx 115$ parts by weight per hundred parts by weight of water [53]. MSH is an important inorganic substance having wide application in the fields of agriculture, medical, dosimetric and luminescence studies [42, 54].

![Figure 2.1: The structure of epsomite projected along (a) [100] (red) O; (white) H; (green) Mg; (yellow) S](image)

Goslarite (ZnSO$_4$.7H$_2$O) white hydrated crystal with molecular weight and density 287.5 g and 1.96g/cm$^3$ respectively, possesses wide range of applications in the field of
telecommunication, solar systems for solar energy storage, coagulation bath for rayon and optical information storage devices. ZnSO$_4$.7H$_2$O, Zinc sulphate heptahydrate (ZSH) belongs to the family of inorganic non linear optical crystal (NLOs) [50, 51]. The unit cell parameters was found to be $a = 11.728$ Å, $b = 11.973$ Å and $c = 6.772$ Å [55]. Figure 2.2 shows the atomic structure of ZSH. Goslariteis is used to supply zinc in fertilizers, in making lithopone, in electrolyte for zinc plating, as a mordant in dyeing, as a preservative for skins and leather.

These two minerals crystallize in the orthorhombic crystal system with tetramolecular unit cells having the space group P2$_1$2$_1$2$_1$. The structure consists of an octahedron formed by Zn$^{2+}$/ Mg$^{2+}$ bonded to six water (H$_2$O) molecules and a tetrahedron formed by S$^{6+}$ ion bonded to four O$^{2-}$ ions. One additional water molecule participates in linking to these structural elements with a network of weak hydrogen bonds. This interstitial seventh water molecule is easily lost at nearby ambient temperature to leave the material hexahydrated.

Although, goslarite and epsomite are orthorhombic and melanterite (FeSO$_4$.7H$_2$O) is monoclinic. The melanterite structure consists of linearly arranged polyhedra linked via H bonds in a corrugated, repeating layer of $M1$-SO$_4$-$M2$-SO$_4$ polyhedra. Copper sulphate pentahydrate, CSP (CuSO$_4$.5H$_2$O) familiarly called as Chalcanthite crystallize in triclinic structure with Space Group: P1 [56, 57]. Atomic structure of CuSO$_4$.5H$_2$O is shown in the figure 2.3. It has the density and molecular weight of about 2.278g/cm$^3$ and 249.68 g respectively. The habit of CSP crystal is a combination of pinacoids [58].
Figure 2.2: Atomic structure of ZnSO₄·7H₂O

Copper atoms in the CSP structure are octahedrally coordinated by four oxygen atoms of water molecules and two oxygen atoms of sulphate groups. The structural motif of CuSO₄·5H₂O is formed by zig-zag three dimensional [Cu(H₂O)₄(SO₄)] chains oriented parallel to the (1 1 0) plane. They are formed due to the hydrogen bonding of H₂O molecules with Cu atoms, the fifth free H₂O molecule, and the oxygen atoms of sulphate groups [56, 57]. Copper sulphate is a very versatile chemical with range of uses in agricultural industry. The metallurgical industry uses large quantities of copper sulphate as an electrolyte in copper refining, for copper coating steel wire prior to wire drawing and in various copper plating processes. The mining industry has found its application as an activator in the concentration by froath flotation of lead, zinc, cobalt and gold ores. The printing trade takes it as an electrolyte in the production of electrolyte and as an etching agent for process engraving. The paint industry uses it in anti-fouling paints and it plays a part in the colouring of glass. These are just some of the examples of usages of
copper sulphate. Today, there is hardly an industry found that does not have some small use for this man-made chemical.

![Atomic structure of CuSO₄·5H₂O](image)

**Figure 2.3: Atomic structure of CuSO₄·5H₂O**

### 2.1.2. Review on metal sulphate single crystals

MgSO₄ crystallizes in a large number of different hydrated forms at different working concentrations and temperatures [4, 59-62].

A previous theoretical study identified magnesium sulfate heptahydrate (MgSO₄·7H₂O) as a promising thermo-chemical tool for long-term heat storage, by means of the following reaction:

\[
\text{MgSO}_4 (s) + 7\text{H}_2\text{O (g)} \leftrightarrow \text{MgSO}_4 \cdot 7\text{H}_2\text{O (s)} + \text{heat}
\]

The theoretical storage density of MgSO₄·7H₂O is 2.8 GJ/m³ [63], which offers a more compact way of storing energy for the same volume when compared to water (0.25 GJ/m³ in the temperature range 25–85°C). Additionally, MgSO₄·7H₂O is cheap, nontoxic, and noncorrosive. For these reasons, MgSO₄·7H₂O was studied as a possible thermochemical tool for solar seasonal heat storage.
Ramalingom et al. [64] have studied the urea doped epsomite crystal at low temperature by slow cooling technique. They found that the addition of urea to the mother liquor of epsomite which increases the metastable zone width consequently the structure of the epsomite crystal structure changed from orthorhombic into tetragonal. The pure epsomite crystals have been grown at low temperature from aqueous solutions. S. Ferdous and J. Podder [65] reported the effect of KCl dopant on the properties of epsomite single crystals. The addition of KCl is found to increase the superiority of the crystals. The increasing in the superiority of the epsomite crystal in presence of KCl is due the completion of trace metal ion with Cl$^-$ ion. The dielectric studies showed that KCl doped epsomite possesses low dielectric constant and low dielectric loss, which could be suitable to electro–optic applications.

Encarnacio’n Ruiz-Agudo et al. [62] studied the effect of various organic additives on the growth and properties of epsomite single crystals. Phosphonates seem to be the most effective additives for the control of epsomite crystallization. The mechanism of additive-epsomite crystal interaction seems to be ruled by certain factors such as the size and charge of the additive molecules and the structural fit of the organic molecule with a particular crystal face. However, the high number of water molecules on epsomite {110} faces in comparison with other faces of the crystal makes the interaction, primarily electrostatic, not highly selective.

The presence of foreign particles in the growth media has long been recognized in changing the growth habits of crystals [66, 67]. Jibbouri et al. [67] presented the influence of different additives (KCl, K$_2$SO$_4$, NaCl and MgCl$_2$) on the crystallization kinetics of epsomite.
The pure zinc sulphate crystals were grown at low temperature from aqueous solutions [55,68,70]. Crystallization of heptahydrate sulphate material such as zinc vitriol (ZnSO₄·7H₂O) of high purity has become an important field of research for both scholastic and engineering applications in various areas like medical, agricultural and chemical industry [41,42]. X-ray diffraction analysis of ZSH were explained by several authors [55, 70].

Studying the crystallization of zinc sulphate heptahydrate single crystals (ZSH), Saha et al. [70] showed that the grown crystal is thermally stable upto 70°C. From the UV spectrum, the grown crystal is found to be transparent in the UV region and it could be a useful tool for optoelectronic applications in visible and infrared region.

Single crystal of Zinc sulphate doped with Magnesium sulphate, a nonlinear material, was grown from aqueous solution by slow evaporation method at room temperature [69]. Mixed crystals of ZSH and MSH were grown by slow evaporation method by Premkumar et al. Enhancement of thermal stability was observed for mixed crystals [71].

Madhurambal et al. [72] have successfully reported the growth of semi-organic nonlinear optical crystal urea-thiourea zinc chloride (UTZC), by slow evaporation technique, at room temperature. J. Ramajothi et al. [73] reported the growth and characterization of tris thiourea zinc sulphate. Single crystals of Zinc thiourea chloride, Zinc thiourea sulphate and Bisthiourea cadmium chloride were grown and characterized by N. R. Dhumane [74].

A study on the growth and characterization of pure, Cd²⁺ and Cu²⁺ doped BTZS single crystals [75] showed the excellent growth characteristics and properties of the
grown crystals makes it suitable for photonic and device applications. Sagadevan Suresh *et al.* [76] have grown the l-valine zinc sulphate single crystal by slow evaporation technique. The dielectric studies show the dielectric constant and dielectric loss decrease exponentially with frequency at different temperatures.

Mahadevan and his co-workers have reported specific refraction measurements [77] and Debye temperature determination [78] on mixed crystals of MgSO₄·7H₂O and ZnSO₄·7H₂O and nucleation studies on mixed crystals of NiSO₄·7H₂O, MgSO₄·7H₂O and ZnSO₄·7H₂O [79-81] and on NiSO₄·7H₂O crystal doped with MgSO₄·7H₂O and ZnSO₄·7H₂O [82].

Ethylene Diamine Tetra Acetic acid (EDTA) doped copper sulphate pentahydrate (CSP) were grown for five different parent-dopant combinations using slow solvent evaporation method at 300 K. The dopant EDTA is also known as artificial amino acid and it is a hexa dentate ligand. It binds through the four oxygens and two nitrogens of EDTA to the central metal copper ion [83] which enhances the SHG efficiency of CSP.

Large single crystals of copper sulfate pentahydrate CuSO₄·5H₂O of optical quality have been grown and their transmission spectra were measured. The crystal thermal stability is investigated and the onset temperature of decomposition is determined to be 41.6°C. A study of absorption spectra of CuSO₄·5H₂O in the frequency range of (5-20)×10³ cm⁻¹ was carried out by Manomenova *et al.* [84].

Thermal stability is an important property of CuSO₄·5H₂O crystals since for the devices using optical filters operate in certain temperature ranges. The CuSO₄·5H₂O dehydration kinetics was investigated [85-87] to find that CSP decomposes in three stages. D. Liu, F.G. Ullman investigated the raman spectra of CSP single crystals [88].
Pure and doped morenosite single crystals have been grown at low temperatures from aqueous solutions [49,89,90]. Lattice Vibration and thermal parameters of $\text{Ni}_x\text{Mg}_{1-x}\text{SO}_4\cdot7\text{H}_2\text{O}$ single crystals was studied by Theivanayagom.M and Mahadevan.C [89]. Ptasiewiez-Bak et al. [91] have determined the charge density distribution in $\text{NiSO}_4\cdot7\text{H}_2\text{O}$ single crystals. In this, the $\text{SO}_4$ group in $\text{NiSO}_4\cdot7\text{H}_2\text{O}$ may be considered similar to the $\text{PO}_4$ group (having tetrahedral geometry) in $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP) and $\text{KH}_2\text{PO}_4$ (KDP). Single crystals of Glycine Lithium Sulphate (GLS) with high degree of transparency were grown from aqueous solution by slow evaporation technique by Suresh et al. [92].

Investigations on non linear optical crystal ADP doped with some inorganic compounds like ferrous sulphate, nickel chloride and cuprium chloride have been done by Maruthi et al. [93] Presence of $\text{Fe}^{3+}$, $\text{Cu}^+$ and $\text{Ni}^{2+}$ ions has resulted in decreased microhardness value. Dielectric constant and dielectric loss decreases with frequency, results in the grown crystals prove to be a useful candidature for many applications.

2.2. Introduction, significance and review on aminoacids doped crystals

2.2.1. Introduction

Second order nonlinear optics (NLO) is widely used to convert the frequency of coherent sources. Applications such as laser based imaging, communication, remote sensing and counter measure system require improved nonlinear optical materials to accomplish such a material conversions. A strong need continues to exist for lower cost, more efficient, higher average power materials for optical parametric amplifier operation and second harmonic generation (SHG) throughout the blue near UV spectral regions.
Another area of growing need is materials for birefringent, phase matched optical parametric oscillators (OPO) for the generation of broadly tunable mid-wave and long wave infrared radiation. Intense attention has been paid to inorganic materials showing the second order nonlinear optical effect because of their higher nonlinearity. Among the nonlinear phenomenon, frequency doubling, frequency mixing, optical phase conjugations and electro-optic modulations are important in the field of optical image storage and optical data storage [94–96].

Aminoacid group of crystals exhibit excellent nonlinear optical and electro-optical properties. Reports are available in literature on the doping of aminoacids in technologically important crystals and the enhancement of the material properties like nonlinear optical and ferro electric properties. For example, enhancement of Second harmonic generation (SHG) efficiency has been reported in L-arginine doped KDP crystals [97]. Kumaresan et al (2008) reported the doping of aminoacids (l-glutamic acid, l-histidine, l-valine) with KDP and studied its properties [98]. The effect on various properties of l-threonine, dl-threonine and l-methionine admixture Triglycine Sulphate (TGS) crystals were studied and the authors reported that the admixture TGS crystals have different properties compared to pure TGS crystal [99].

Many members of natural aminoacids are individually exhibiting the nonlinear optical properties because they have a donor NH$_2$ and acceptor COOH group and the intermolecular charge transfer is also possible. Mostly natural aminoacids such as arginine, histidine, lysine and γ glycine are evidently showing NLO activity because of the presence of -COOH group and -NH$_2$ group. Therefore, aminoacids may be used as dopants and it was observed that there is enhancement in the material properties such as nonlinear optical (NLO) and ferro electrical properties [100–104].
2.2.2. Significance of aminoacid doped crystals

Aminoacids, the base units of polypeptide and proteins, are vital functional groups in almost all neuro transmitters and in many other biological systems. It is very essential to study the behavior of aminoacids in solution at the interface, and in the crystalline state to understand the interaction with these receptors, and their mechanism of action [105].

The nonlinear optical properties of large organic molecules and polymers have been the subject of extensive theoretical and experimental investigations during the past two decades [106,107]. The organic NLO materials play an important role in second harmonic generation, frequency mixing, electro-optic modulation, optical parametric oscillation, optical bistability etc. [108,109]. In the search of new materials aminoacid family single crystals are gaining importance due to their second harmonic generation applications. The importance of aminoacids for NLO application lies on the fact that the molecules are of dissymmetric [110,111] space group. The dipolar nature (zwitterionic) exhibits peculiar physical and chemical properties in aminoacids, thus making them ideal tool for NLO applications.

Nonlinear optics has emerged as one of the most attractive fields of current research in view of its vital application in areas such as optical modulation, optical switching, frequency shifting and optical data storage for the technological development in telecommunication and signal processing [112,113]. Semiorganic nonlinear optical (NLO) crystals formed by aminoacids with an inorganic ligand possess combined advantages of high optical nonlinearity of organic aminoacids and favorable mechanical and thermal properties of inorganic solids. The importance of aminoacids in NLO applications is due to the fact that all aminoacids except glycine contain a chiral carbon atom and crystallize in noncentrosymmetric space group. Therefore, they are potential
candidates for second harmonic generation, optical parametric amplifiers (OPA) and optical parametric oscillators (OPO).

As a result the recent research is concentrated primarily on organic compounds owing to their large nonlinearity. The NLO properties of organic molecules have been investigated widely due to their rapid responses in electro-optic effect and large second or third-order hyper polarizabilities compared to inorganic NLO materials. Crystalline salts of aminoacids are one of the directions for searching new nonlinear optical materials in which much attracted were salts of l-arginine, l-histidine and l-threonine [114-117]. Crystals capable of generating second harmonics must have a unit cell with no centre of inversion and this requirement is met by the crystals of pure aminoacids because these molecule themselves are asymmetric [111,119]. A number of L-histidine compounds exhibiting the optical properties in organic crystals like L-histidine acetate [120], L-histidinium trichloraacetate [121], L-histidinium trifluoroacetate [122], L-histidinium tetrafluorophthalate [123] etc were reported. Studies on mechanical and dielectric properties of L-Phenylalanine benzoic Acid single crystal were carried out by Suresh et al [124].

2.2.3. Review on aminoacid doped crystals

The salts of aminoacids like L-arginine, L-histidine [119,125] are reported to have high second harmonic conversion efficiency. In other words they have the advantages of both organic and inorganic crystals in terms of their physicochemical properties. Since the theory of double-radical model (organic conjugated molecular groups are included in the distorted polyhedron of coordination complex) was introduced in 1997 [126], metal-organic coordination compounds have attracted much more attention due to their considerable high NLO coefficients (contrast to inorganic materials), stable physico-
chemical properties and better mechanical intention (contrast to organic materials). With the guidance of this theory, many metal organic coordination materials with good NLO effect have been designed and synthesized [127]. The metal-organic coordination complexes can also provide the following advantages: i) an enhancement of the physico-chemical stability. ii) the breaking up of the centrosymmetry of the ligand in the crystal, and iii) an increase in NLO intensity, via metal-ligand bridging interactions. The central metal ion (together with its hybrid electronic orbital) not only offers a certain anisotropic field to keep the NLO active chromopher ligands in a favourable acentric arrangement but also involved in the NLO processes. Most importantly, the material in question must be crystallographically noncentrosymmetric (NCS). Mathematically, it has been known for some time that only a NCS arrangement of atoms may produce a second-order NLO response [128]. Several new complexes incorporating the aminoacid have been recently crystallized and their structural, optical and thermal properties have been investigated [129]. Hence it may be useful to synthesize the aminoacid complexes with other carboxylic acids and study their properties.

A number of L-histidine compounds exhibiting the NLO properties in inorganic crystal, namely, L-histidine chloride monohydrate [130], L-histidine tetrafluoroborate [131], L-histidine hydrochloride monohydrate [132], L-histidine hydrofluoride dihydrate [133], L-histidine bromide [134], L-histidine nitrate [135] etc. were reported. A novel method of growing L-histidine hydrochloride monohydrate (LHC) single crystals was developed by Robert and his Coworkers [136]. The crystals were grown in aqueous solution by unidirectional growth technique. Nonlinear optical studies were carried out for the grown crystal and second harmonic generation efficiency was found to be three times that of KDP crystals. Effects of the addition of L-lysine monohydrochloride dihydrate on the growth and various properties of ADP single crystal grown by the slow
cooling method have been studied by Rajesh et al [137]. Dielectric studies reveal that the grown crystal has dielectric constant slightly higher than the pure ADP. Higher hardness value is obtained for the L-lysine monohydrochloride dihydrate-added ADP than the pure ADP crystal.

Rajesh et al. [138] have studied the effect of ammonium malate on growth rate, crystalline perfection, structural, optical, thermal, mechanical, dielectric and NLO behaviour of ammonium dihydrogen phosphate crystals. Bulk single crystals of L-HBr have been successfully grown by the evaporation and temperature lowering technique from aqueous solution by Rajendran et al. [145]. It seems to be a polar crystal in which the growth rate in the (1 0 0) direction is much greater than the other direction such as (0 1 1), (0 1 1) and (0 0 1).

A novel method of growing Dichlorobis (L-proline) Zinc (II) (DCBPZ) single crystals was developed by Anandha Babu.G and Ramasamy.P [139]. Optical quality single crystals of DCBPZ were grown using solution growth techniques. The SHG relative efficiency of DCBPZ is three times that of KDP hence it seems to be a promising material for NLO applications.

Investigation on the physicochemical properties of L-histidinium dinitrate (LHDN) was carried out by Aruna et al [140]. LHDN has a wide transparency window from 260 to 1700nm, which highlights their prediction of application as NLO materials. Studying the infrared vibrational spectra of L-histidinium dihydrogen orthophosphate orthophosphoric acid (LHP), Espinosa et al. [141] showed that the use of polarized IR reflectivity spectroscopy is used to determine the symmetry species of the various modes.
of vibration in LHP, as well as the observation of both the lattice modes and the internal vibrations.

A study on the growth and characterization of nonlinear optical L-histidinium dihydrogen phosphate (L-HDP) single crystal [142] showed that the SHG of the grown crystal were found to be greater than that of KDP. The morphology of L-HDP shows that the crystal grows faster along the a and b directions than along c direction.

Crystal structure, vibrational spectra and theoretical studies of L-histidinium dihydrogen phosphate-phosphoric acid has been investigated by Ben Ahmed et al [143]. It crystallizes in the non-centrosymmetric space group P2$_1$ of monoclinic system. The study indicates that in acid-base hybrid crystals, hydrogen bonds play an important role not only in the creation of crystal structure and its stability, but also in the enhancement of the polarizability and hyperpolarizability of the crystal.

A well known semiorganic single crystal like L- histidine tetrafluoroborate (L-HFB) has been successfully grown by Marcy et al. [144]. And it was found that L-HFB has higher NLO properties than L-arginine phosphate monohydrate (LAP). The growth kinetics, linear and non-linear properties of L-HFB was reported by Aggarwal et al. [131] and Rajendran et al [39]. Hydrogen bonding and thermal vibrations in crystalline phosphate salts of histidine and imidazole were reported for the first time by Blessing [147]. Roman et al. [148] reported the spectroscopic and structural study of L-histidinium perchlorate. Karle et al. [149] studied the reaction of L-histidine with squaric acid (H$_2$C$_2$O$_4$). Reena Ittyachan and P.Sagayaraj [150] have reported for the first time the growth of L-histidine bromide single crystal by slow evaporation technique and various characterization studies were made by them, reveals that the crystal possess good SHG efficiency.
Single crystal growth of the organic nonlinear optical crystal, L-arginine trifluoroacetate (LATA) is reported by Sun et al [151]. Low temperature solution growth method is employed for the growth of bulk single crystal. The SHG intensity of LATA is found to be 2.5 times as that of KDP shows that the crystal is a potential NLO material. Bulk single crystal LATA of dimension 57mm×5mm×3mm has been grown by temperature lowering technique by Arjunan et al. [152] reveals that LATA has a good transparency of 85% with a lower cutoff wavelength at 232 nm.

Single crystals of organic nonlinear optical material of pure and Mg\(^{2+}\) substituted L-tartaric acid-nicotinamide (LTN) were successfully grown by slow evaporation method at room temperature [153]. NLO studies reveal that the SHG efficiency of the grown crystals is found to be increased in the presence of magnesium ions. The results obtained from the study indicates that LTN is not only a potential NLO material but also a promising low permeability dielectric material, expected to be useful in the microelectronics industry.

### 2.3. L-arginine doped crystals

#### 2.3.1. Importance of L-arginine doped crystals

L-arginine is one of the essential aminoacids widely distributed in biological substances. The functions and role of L-arginine molecules in living matter are characterized by the strong basicity of the guanidyl group. As a result, L-arginine forms a number of salts with organic and inorganic acids with nonlinear optical properties [115,154]. L-arginine is probably the most promising common naturally occurring aminoacid to form a stable zwitterions in the gas phase due to its extremely basic guanidine side chain \([(CH_2)_3-NH-C-(NH_2)NH]\). The side chain of arginine is significantly
more basic than the N-terminus. This should stabilize the arginine zwitterions relative to the simple neutral structure. The zwitterion form can be stabilized by the presence of an additional charge, thereby forming a salt bridge. Due to its zwitterionic nature and the search for effective NLO materials, reveals that the L-arginine based crystals are the potential materials with excellent optical, thermal and mechanical properties [155]. A systematic study on the single crystal growth and characterization of many of these salts like L-arginine hydrofluoride (LAHF) [156], L-arginine hydrobromide monohydrate (LAHBr) [157], L-arginine hydrochloride monohydrate (LAHCl) [158], L-arginine trifluoroacetate (LATF) [159], L-arginine acetate (LAAC) [160,163], L-arginine hydrochloride [161], L-arginine perchlorate (LAPCl) [162], L-arginine diiodate [164,165] L-arginine iodate [166] were undertaken by many of the researchers for different period of time.

2.3.2. Review on L-arginine doped crystals

Mahadevan and his co-workers [167,168] have reported the possibility of reducing the dielectric constant value by adding simple organic molecules like urea and L-arginine to KDP. Single crystals of bis(thiourea) zinc chloride (BTZC) doped with basic aminoacid L-arginine were grown successfully by slow evaporation method at ambient temperature. The doped crystals were optically better and more transparent than the pure ones. Introduction of L-arginine in the crystal lattice creates ionic vacancy as L-arginine exists as zwitterion in the solid state. The dislocation motion is obstructed by these defects, which increases the hardness of the crystals with doping. [169].

Studies on the growth and characterization of nonlinear optical crystal zinc tris(thiourea) sulphate in the presence of L-arginine [170] showed that the influence of
organic impurity on the growth and physical properties of bulk ZTS single crystals. Impurities play a key role in changing the morphology of the crystals.

P. V. Dhanaraj et al. [171] carried out a study on the characterization of potassium dihydrogen phosphate single crystals with L-arginine monohydrochloride (LAHCl) as additive shows that the presence of LAHCl increases the growth rate and improves the quality of the crystal with highest transparency and also shows that LAHCl-doped KDP crystal is found to be mechanically harder than pure KDP.

The metastable zonewidth and induction period values of pure and L-arginine added zinc thiourea chloride (ZTC) crystals have been determined. Also, it was found that there is an improvement of SHG efficiency due to L-arginine doping was observed and is comparable with that of KDP [172].

2.3.3. Review on metal ions doped with L-arginine based crystals

Single crystals of pure, Cu$^{2+}$ and Mg$^{2+}$ doped L-arginine acetate (LAA) were grown by Praveen Kumar et al [173]. Inorder to improve the device characteristics of LAA crystals, metal dopants of Cu$^{2+}$ and Mg$^{2+}$ were incorporated into the parent crystals. Thermal studies concluded that the metal dopants have not altered the thermal stability of the molecules. NLO studies proved that the Cu$^{2+}$ and Mg$^{2+}$ metals have increased the efficiency of pure LAA.

Cu and Mg doped single crystals of L-arginine diphosphate (LADP) are grown by slow evaporation method in the period of 30-45 days by Joseph Arul Pragasam et al [174]. The NLO studies confirm that the grown crystals are non-linear in nature and the metal substitution has enhanced the non-linearity of the crystals. Natarajan et al. [175] carried out a study on Li-doped L-arginine acetate single crystals by the solvent
evaporation technique. The effect of Li-doping on the growth, structural and optical properties of LAA crystal has been investigated.

2.4. Scope of the present investigation

The ever increasing demand for highly efficient nonlinear optical (NLOs) crystals for visible and ultraviolet regions is extremely important for laser and material processing. In this context, the design and growth of single crystals suitable for such requirements, assumes centre stage. Literature shows only few reports on aminoacid doped metal sulphate single crystals. Keeping this in view, attempts were made to grow defect free L-arginine doped metal sulphate single crystals (MgSO$_4$.7H$_2$O, ZnSO$_4$.7H$_2$O, CuSO$_4$.5H$_2$O and FeSO$_4$.7H$_2$O) by using slow evaporation method. L-arginine is used as dopant in different concentration such as 0.01, 0.03 and 0.05 mole %.

Therefore the present investigation was aimed at:

(i) Identifying the crystal structure by Powder X-Ray diffraction analysis

(ii) Confirming the protonation of the amino group (-NH$_2$) and the mode of vibration of different molecular group using FT-IR spectra

(iii) Characterization of grown crystals also includes UV-Vis-NIR and NLO studies.

(iv) Study of thermal behaviour of the grown crystals.

(v) Determination of microhardness values.

(vi) Measurement of dielectric loss, dielectric constant and electrical conductivity of the grown crystals.

All the results are discussed in detail in the following chapters.