Growth, Characterization, Crystal structure and DFT studies on some novel Semiorganic Crystals for NLO applications

SYNOPSIS

Nonlinear optics (NLO) is a forefront of current research because of its importance in providing the key functions of frequency conversion, light modulation and optical memory storage for the emerging technologies in areas such as telecommunications, signal processing and optical interconnections. In recent years, there has been extensive research on the growth of nonlinear optical materials because of their wide applications in optoelectronics.

Most of the organic crystals have inadequate transparency, poor optical quality and a low laser damage threshold. Moreover, growth of a bulky large-sized single crystal is difficult for device applications. Inorganic crystals have excellent mechanical and thermal properties but they possess relatively modest nonlinearity. Due to the above reasons, a lot of research have been carried out on semiorganic materials which have combined properties of both organic and inorganic materials. The semiorganic materials are more suitable for device fabrication due to the wide transparency window and high second harmonic generation efficiency with mechanical and chemical stability.

Hence, the researcher has preferred to focus on semiorganic compounds due to their large nonlinearity, high resistance to laser damage threshold, low angular sensitivity and good mechanical hardness. In the semiorganic crystals, the organic ligand shows higher nonlinear optical property and the metallic part focuses on mechanical property and the electrical conductivity.

Now-a-days, amino acids are most suitable organic materials for nonlinear optical applications because they are of dipolar nature due to the presence of a protonated amino group (NH_3^+) and deprotonated carboxylic group (COO^-). Glycine is the simplest amino acid in terms of structure. Despite its simple structure, it has many important applications. It is a potential active pharmaceutical ingredient (API) for the pharmaceutical industry. It has an important role as a neurotransmitter in our central nervous system and it possesses interesting nonlinear optical properties for photonics and optoelectronics. Glycine and its derivatives have attracted much interest due to their prospective applications as nonlinear optical materials. Glycine exists in neutral form in the gas phase but as zwitterions in both the crystal and solution state. It has three known polymorphs, namely α-, β-, and γ-glycine polymorphs. Due to its relatively simple structure, the existence of multiple polymorphs, and its wide potential applications, glycine is often investigated as a model compound in studies of crystal growth. The α-glycine crystallizes in the centrosymmetric, monoclinic structure with space group $P2_1/n$. The lattice parameters of α-glycine are a = 5.105 A˚ , b = 11.969 A˚, c = 4.464 A˚ and β = 111.697. The unit cell contains 4 molecules.

The 12th group metal oxides are considered for inorganic material, particularly, ZnO, for its unique optical, semiconducting, piezoelectric and magnetic properties. ZnO has direct band gap and this wide band gap material covers ultraviolet to infrared energy range. This wide optical window from UV to IR region is the most required condition for NLO materials. Glycine forms several new compounds with other organic as well as inorganic materials. Recently, several complexes of glycine have been reported. But the provided literature survey clearly indicates that the interaction of glycine and zincoxide with water as a solvent remains unexplored so far.

In the present work, for the first time with reference to literature, the semiorganic crystals of α-glycine, zincoxide and ternary additive such as one of the alkali metals, transition metals and dyes are grown from aqueous solution by the slow evaporation technique at room temperature. The selected additives are alkali metals (Lithium, Sodium, Potassium, Rubidium and cesium), transition metals (Manganese, Iron, Cobalt, Nickel and Lead) and dyes (Aniline blue, Brilliant green, Crystal violet, Methyl red and Rhodamine red). The addition of the above said metal elements onto α-glycine is experimentally executed and its physicochemical properties like optical enhancements, vibrational signatures, mechanical strength, thermal stability, electrical conductivity and nonlinearity with respect to its respective additives are extensively discussed. The quantum chemical calculations using Density Functional Theory (DFT) are carried out on molecular structure analysis, vibrational analysis, natural bond orbital (NBO) studies and first order hyperpolarizability study to validate the experimental findings of the grown crystals.

Chapter - I explains the rationale behind the work which is undertaken for the research. The retro of the work broadly elaborates the similar type of the research works previously reported (i.e.) literature survey. The basic physical and chemical properties of host element α-glycine and the additives are discussed. A review on nonlinear optics is given in this chapter.

Chapter - II elaborates the introduction to crystals and types of crystals. The various methods of crystal growth are explained in this chapter with an importance to solution growth technique. The experimental set up and experimental procedure for growing the pure α-glycine, ZnO added α-glycine and ZnO with ternary element added α-glycine are clearly explained here. This chapter deals with an overview of various instrumentation techniques and their principles which are used to characterize the grown crystals. The computational methods and theoretical concept of density functional theory (DFT) have been explained thoroughly.

Chapter - III deals with the experimental and theoretical structural and vibrational properties, natural bond orbital (NBO), first order hyperpolarizability, the enhancement of mechanical, thermal, electrical, linear and nonlinear optical properties of α-glycine (GLY) and glycine.zincoxide (GZO) crystals.

Glycine is the simplest amino acid and is the only amino acid that is not optically active. It has an organic carboxylic acid group and an amino group attached to a saturated carbon atom, where the saturated carbon atom is un-substituted, rendering it optically inactive. Glycine has no enantiomers because it has two hydrogen atoms attached to the central carbon atom. Only when all four attachments are different then only enantiomers can occur. Enantiomers are chiral molecules that are mirror images of one another. Furthermore, the molecules are non-superimposable on one another. This means that the molecules cannot be placed on top of one another and give the same molecule. Chiral molecules with one or more stereo centres can be enantiomers and are optically active. Since glycine is an achiral and centro-symmetric amino acid, it has no stereo isomers and it is optically inactive. When the non centro-symmetric inorganic salt ZnO is added with glycine in the growth solution, then the grown α-glycine single crystal possesses an improved optical, mechanical and physical properties.

From the EDAX analysis, powder X-ray diffraction studies and single-crystal X-ray diffraction analysis, it is predicted that, the as-grown crystals belong to α-glycine single crystal with the monoclinic crystal system having space group P21/n. The grown semiorganic crystal GZO possesses the good crystalline nature over the α-glycine crystal (GLY). In the GLY crystal the (0 4 0) plane has maximum intensity which is very well matched with JCPDS file no: 32-1702 and with ZnO additive crystal (GZO) the same (0 4 0) plane has maximum intensity with very high crystallinity. The increased intensity of the maximum intensity peak (0 4 0) for GZO crystal is due to the incorporation of ZnO in the α-glycine crystal which is also the reason for enhancement of optical activity of glycine. In all other earlier reported work, due to the addition of additive molecules, either the polymorphs of the glycine crystals had been changed or the dopant molecules entered into the crystal lattice and changed the crystal structure of glycine. In the present work, though the inclusion of ZnO altered the external morphology, the basic crystal structure of α-glycine single crystal remains unaltered. It is concluded that, the additive ZnO occupies the interstitial space of the glycine crystal without disturbing the crystal structure of α-glycine.

The grown ZnO added α-glycine (GZO) semiorganic crystal, inherently possesses third order nonlinear properties due to its centro-symmetric nature. The second order nonlinearity is also measurably increased in this centro-symmetric crystal due to the addition of ZnO. This increased second order nonlinearity is experimentally and theoretically verified by Kurtz and Perry technique and by first order hyperpolarizability studies respectively. The increased third order nonlinearities of the GZO crystal over GLY crystal is studied by Z-scan technique. The peak followed by valley-normalized transmission obtained from this study indicates the negative sign for the nonlinear refractive index (self-defocusing) of GLY and GZO crystals. The experiment has revealed that the titular crystals exhibit the reverse saturable absorption (RSA) making the crystals as promising candidates for optical limiting applications.

The optical properties are determined using UV-Visible spectroscopy. The transmittance is found to be poor for pure glycine (GLY). But for zinc oxide additive glycine (GZO) it is found to be high and it possesses good transparency in the near UV, visible and near IR regions. This wide optical window is the most desirable property for NLO applications. The linear refractive index and the band gap values are calculated. The photoluminescence analysis is carried out for both GLY and GZO crystals to study the emission property of the grown crystals. All the grown crystals have blue emission with high PL intensity than the pure GLY crystal.

The vibrational characteristics present in the grown crystals have been studied using FTIR spectra and micro-Raman spectra. The calculated vibrational frequencies of the title crystals are assigned on the basis of potential energy distribution (PED) calculation with VEDA 4.0 program. The observed and stimulated FTIR and micro - Raman spectra of both glycine (GLY) and glycine.zincoxide (GZO) crystals are very well correlated with each other.

The mechanical strength of the grown crystals is assessed by Vicker's microhardness test. The strength of the semiorganic crystal (GZO) is increased because of the addition of the metal ions in the GLY crystal. The thermal stability of the material is elucidated from the TG-DTA analysis. From the TG-DTA curve, it is observed that the grown crystals are stable up to 270ºC. The Laser Damage Threshold (LDT) value of the GZO crystal is twice that of the standard KDP crystal.

The highly increased electrical conductivity of GZO over GLY is predicted by impedance analysis of the grown crystals. The lower values of dielectric constant and dielectric loss at high frequencies have indicated an enhanced optical quality with lesser defects of the crystal samples which is of vital importance in non linear optical materials in their applications.

Chapter - IV discusses the further enhancement of second order nonlinearity of the binary GZO crystal for second harmonic generation (SHG). To achieve this property, a third element is added with ZnO and glycine. The ternary mixed crystal of sodium, ZnO and α-glycine is grown successfully from aqueous solution by slow evaporation method. The structural studies predict that the grown crystal belongs to α-glycine single crystal with monoclinic system having space group P21/n. The additives occupy the interstitial space of the crystal without altering the basic structure of glycine. The molecular structure analysis, IR, Raman vibrational analysis and NBO studies using DFT very well support the experimental results. The ternary mixed crystal significantly increases the linear and nonlinear optical activities which is also elucidated by the DFT calculation of first order hyperpolarizability. The SHG efficiency of sodium, ZnO and glycine mixed crystal is 1.3 times that of the standard KDP crystal and it is found to be higher than other centrosymmetric crystals. The additives increase the mechanical hardness, thermal stability and electrical conductivity of the α-glycine crystal. The remarkable increase in electrical conductivity of the ternary mixed glycine crystals makes it as a promising material in the pharmaceutical industry also. The presence of both second and third order nonlinearities of this semiorganic crystal makes it, a very novel material and a suitable material for NLO devices. In summary, the present study indicates that the ternary mixed crystals of ZnO with sodium added α-glycine (GZO-Na) is a promising material for linear and nonlinear optical applications.

Chapter - V discusses the effect of Lithium (Li) and Potassium (K) with ZnO added glycine crystals. The ternary mixed crystals of one of the alkali metals Li and K with ZnO and α-glycine are grown successfully from aqueous solution by slow evaporation method. The structural studies predict that the grown crystals belong to α-glycine single crystal with monoclinic system having space group $P2_1/n$. The additives occupy the interstitial space of the crystal without altering the basic structure of glycine. The ternary mixed crystals significantly increase the optical activity, mechanical hardness and electrical conductivity of the α-glycine single crystal. The molecular structure analysis, IR, Raman vibrational analysis, NBO studies and first order hyperpolarizability studies using DFT very well support the experimental results. The remarkable increase in electrical conductivity of GZO-K crystal is also theoretically described by NBO analysis. The presence of good third order nonlinearities, proper electrical conductivity and required dielectric loss of these semiorganic crystals make it as a suitable material for NLO devices.

Chapter - VI describes the effect of Rubidium (Rb) and Cesium (Cs) with ZnO added glycine crystals. The ternary mixed crystals of one of the alkali metals Rb and Cs with ZnO and α-glycine are grown successfully from aqueous solution by slow evaporation method. The structural studies predict that the grown crystals belong to α-glycine single crystal with monoclinic system having space group $P2_1/n$. The additives occupy the interstitial space of the crystal without altering the basic structure of glycine. The ternary mixed crystals significantly increase the optical activity, mechanical hardness and electrical conductivity of the α-glycine single crystal. The molecular structure analysis, IR, Raman vibrational analysis and first order hyperpolarizability studies using DFT are carried out and they very well support the experimental results. The presence of good third order nonlinearities, high electrical conductivity and required dielectric loss of these semiorganic crystals make it as a suitable material for NLO devices.

Chapter - VII gives a detailed account of experimental investigation on structural, vibrational, thermal, mechanical, electrical, linear and nonlinear optical properties of transition metal added glycine.zincoxide crystals. The selected transition metal additives are Manganese (Mn), Iron (Fe), Cobalt (Co), Nickel (Ni) and Lead (Pb). The ternary mixed crystals are grown by the slow evaporation method at room temperature. From the XRD spectra of pure and ternary mixed semiorganic crystals, the variation in peak intensities is observed and also it is illustrated that the additives alter the external morphology but preserve the monoclinic crystal structure of the α-glycine crystal. EDS analysis confirms the presence of the respective ratio of the elementary metal compounds in the grown crystals. The characteristic vibrations of organic functional groups and metal-ligand vibrations are assigned from FTIR and micro-Raman spectra. The mechanical hardness and the thermal stability are enhanced by the metal additives. The electrical studies predict the tremendous increase in the electrical conductivity of the grown crystals. ZnO with cobalt added α-glycine (GZO-Co) crystal shows a inductive reactance which is reported for the first time in α-glycine crystal. The lower values of dielectric loss at high frequencies have indicated an enhanced optical quality with lesser defects of the crystal samples which is a prerequisite condition for a non linear optical materials in their applications.

Chapter - VIII details only the experimental investigation on structural, vibrational, thermal, mechanical, electrical, linear and nonlinear optical properties of dyes added glycine.zincoxide crystals. The selected dyes for additives are Aniline blue, Brilliant green, Crystal violet, Methyl red and Rhodamine red. The ternary mixed crystals are grown by the slow evaporation method at room temperature. From the XRD spectra of pure and ternary mixed semiorganic crystals, the variation in peak intensities is observed and also it is illustrated that the additives alter the external morphology but preserve the monoclinic crystal structure of the α-glycine crystal. EDAX analysis confirms the presence of the respective ratio of the elementary metal compounds in the grown crystals. The characteristic vibrations of organic functional groups and metal-ligand vibrations are assigned from FTIR and micro-Raman spectra. The mechanical hardness and the thermal stability are enhanced by the metal additives. The electrical studies predict the increase in the electrical conductivity of the grown crystals. The lower values of dielectric loss at high frequencies have indicated an enhanced optical quality with lesser defects of the crystal samples which is a prerequisite condition for a non linear optical materials in their applications.

Chapter IX describes the summary of the vital outcomes of the present investigations. The investigated results of the additives added binary and ternary mixed semiorganic crystals of α-glycine are compared and presented in this chapter. The summary of the present work is given below:

- Optically good quality crystals of pure α-glycine, ZnO added binary α-glycine and ZnO with third element added ternary α-glycine crystals are grown from the slow evaporation technique at room temperature.
- Incorporation of metal ions in the host crystal, α-glycine is confirmed using EDS analysis.
- Powder XRD and single crystal XRD reveal that the additives enhance the crystallinity of α-glycine crystal and preserve the monoclinic system.

- The molecular structure of grown crystals is optimized by DFT/B3LYP method using the basis set 6-311++ G(d,p), 6-311G(d,p) and LanL2DZ using Gauss 09 program with Gauss view 03. The calculated structural parameters are very well support the reported values.
- The respective vibrational signatures have been analysed successfully using FTIR and micro-Raman spectra and they are elucidated theoretically by stimulated vibrational spectra on the basis of potential energy distribution (PED) calculation with VEDA 4.0 program.
- The intra molecular charge transfer and stabilization energy of the grown crystals is studied NBO analysis.
- The strong absorption in the UV region and high transmittance in the visible and near IR region for these semiorganic crystals make them a suitable candidate for optical device filters. These semiorganic crystals belong to wide band materials.
- The additives in the α-glycine results in the enhanced intensity of emission spectra in the blue region.
- Increase in hardness value has been observed with the incorporation of respective additives in pure glycine.
- Metal additives in glycine significantly increase the thermal stability and electrical conductivity of the compound.
- First order hyperpolarizability study and second harmonic generation test confirm the second order nonlinearity of the crystals.

- The high magnitude of third order susceptibility for the binary and ternary glycine semiorganic crystals is determined by Z-scan technique.
- The enhanced second and third order nonlinearities are mainly due to the interactions between the additives and glycine molecules.
- The glycine semiorganic crystals hold efficient optical applications in the field of optical switching devices, frequency converters, electro-optic modulators and optical filters.
- Very important novelty in this present investigation is that, ZnO with sodium added α-glycine (GZO-Na) semiorganic crystal possesses both second order and third order nonlinearities. The SHG efficiency of this centrosymmetric crystal is 1.3 times of standard KDP crystal. It possesses high third order nonlinear susceptibility of 9.34E-08 esu.

The results of the present investigations of semiorganic glycine crystals allow abundant scope for further investigations in these materials in future.