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An Overview of Selective Amino acid Based NLO Crystals

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Abstract : Non linear optical (NLO) materials show their own contribution in many fields such as photonics, electronics, medical, artificial intelligence etc., This article is an overview of amino acid based NLO crystals.

1. Introduction

The non linear optical materials gaining vital importance in designing materials and devices due to their NLO properties. It is the backbone material for running various industries such as photonics (optical and electro-optical switching), medical, artificial intelligence etc. due to their wide range of potential and technological applications of frequency mixing, optical storage devices, laser remote sensing, optical modulation, information and image processing in computers, telecommunications, medical diagnostics, robotics etc., So these materials find wide application almost in all fields of science and technology[1-3]. Due to this researchers shown much interest in synthesize inorganic, organic and semiorganic NLO materials.

2. Inorganic materials

Compared to organic materials, inorganic materials are preferred for NLO applications. Some of the inorganic materials such as quartz, potassium dihydrogen phosphate (KDP) , potassium titanyl phosphate (KTP) , lithium niobate ($LiNbO_3$), β-barium borate (BBO) etc shows excellent NLO properties. These are used in SHG devices, parametric oscillators etc., [4-8]. One of the inorganic NLO material barium sodium niobate ($BaNaNb_5O_{15}$) is known as banana which is optically transparent material. It's NLO efficiency is three times greater than that of $LiNbO_3$ [3]. One of the interesting super ionic conducting crystal NASICON (acronym for sodium (Na) Super Ionic Conductor) which is used as solid electrolyte in sodium ion battery. It is also used as phosphors, detectors, immobilization of nuclear waste etc., [9]. Inorganic materials possess very good mechanical strength, thermal stability, transmittance and high electro-optic coefficients. But due to a lack of extended π electron delocalization, the inorganic materials have modest optical nonlinearities.

3. Organic materials

Organic materials show superior NLO properties due to their π conjugated electronic system between donor and acceptors [10-11]. Generally organic crystals are considered as an alternative to inorganic species because of their fast and large non-linear response over a broad frequency range, inherent synthetic flexibility and high optical damage threshold. Some polar organic crystals which form a non - centro symmetric structure exhibited second order NLO properties. Organic materials with very large second order non-linear optical (NLO) susceptibilities have attracted a lot of attention because of their potential use for high frequency electro optic modulation [12-16], frequency conversion and tera hertz (THz) wave generation and detection [17-19]. Such materials offer numerous design possibilities and larger optical nonlinearities, when compared to their inorganic counterparts [20-21].One of the interesting NLO crystal,4-N, N-dimethylamino-4-N-methylstilbazolium tosylate (DAST) shows its SHG efficiency 10 times greater than that Lithium niobate ($LiNbO_3$) and 1000 times greater than that of urea [20].

3.1 Co-crystal

It is the subclass of organic material. Co-crystals are the solids that are crystalline single phase materials composed of two or more different molecular and/or ionic compounds generally in a stoichiometric ratio which are neither solvates nor simple salts. These crystals interact via non-covalent interactions like ionic, vanderwaals, π interactions. The intermolecular interactions and resulting crystal structures can generate physical and chemical properties that differ from the properties of the individual components[22]. Most of the cocrystals are used in pharmaceutical field. Recently some of the co-crystals such as isonicotinamidium picrate, 4-(amino carbonyl) pyridine 4-(amino carbonyl)pyridinium hydrogen L-malate, l-tartaric acid–nicotinamide and d-tartaric acid–nicotinamide synthesized successfully and it shows excellent NLO properties. [23-25].

4. Semi-organic materials

The recent trend of combining the high nonlinear optical coefficients of the organic molecules with the excellent physical properties of the inorganics has been found to be overwhelmingly successful and the research is concentrated on semiorganic materials due to their large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness [26].Some of the semi organic NLO crystals such as Potassium boro succinate, Thio semicarbazide cadmium acetate, Tri-diethyl ammonium hexachloro bismuthate synthesized successfully [27-29].

5. Amino acid based materials

The combination of amino acid based materials exhibit specific features of interest. Aminoacids are considered to be interesting organic materials for NLO devices as they contain donor carboxylic (COOH) group and the proton accept or amino acid (NH_2) groupin them, known as zwitterions which create hydrogen bonds. Due to their dipolar nature, amino acids have improved physical properties that make them ideal candidates for diverse applications [30].The advantage of the organic amino acid materials over in organic counterparts is the high electronic polarizability through high molecular hyperpolarizability.

In this review some selective amino acids of L-alanine and arginine based NLO materials are choosen and analyzed their NLO efficiency.

L- alanine is an alpha and L-type aminoacid. It is easily dissolves in water, slightly dissolves in alcohol and insoluble in ether. It is considered as an fundamental building block of more complex aminoacids which shows strong non linear behaviour. Similarly arginine also shows a strong non linear activity. Few of the L- alainine and arginine based NLO materials are listed in the Table 1.1.

Compound	Lattice parameters & space group	Characteristics
L-Alaninium Maleate [31]	a = 5.588(2) Å, b = 7.380(4) Å, c = 23.699(1) Å , orthorhombic system and the space group is $P2_12_12_1$	• Laser damage energy density was found to be 4.9 GW/cm2. • SHG efficiency is 1.2 times higher than that of KDP.
L-alanine cadmium chloride [32]	a = 16.33, b = 7.31, c = 8.00 Å, cell volume V = 854 Å3, $\alpha = \gamma = 90°$ and $\beta = 116.44°$, monoclinic system with space group C2	• Good optical transparency in the entire visible region with a lower cut of wave length at 200 nm. • SHG efficiency is 0.57 times greater than the value of KDP
strontium metal ion doped L-alanine cadmium chloride [32]	a = 16.352 (± 0.011) Å, b = 7.303 (± 0.005) Å, c = 7.978 (± .006) Å, cell volume V = 851.7(± 1.7) Å3, $\alpha = \gamma = 90°$ and $\beta = 116.62$ (± 0.03)°,	• Good optical transparency in the entire visible region with a lower cut of wave length at 200 nm. • SHG efficiency is 0.82 times greater than the value of KDP

	monoclinic system with space group C2	
Urea L-alanine acetate (ULAA) [33]	a = 5.7971Å, b = 6.0391 Å, c = 12.3276 Å , orthorhombic system and the space group is $P2_12_12_1$ (D_2^4)	• Thermal stability 214°C. Lower cut off wavelength 220 nm. • NLO efficiency is 6.7 mV with reference of KDP 7.0 mV
L-alanine DL malic acid (LADLMA) [34]	a = 5.8115Å, b = 6.0298 Å, c = 12.3185 Å , orthorhombic system and the space group is $P2_12_12_1$	• Thermal stability 217°C. Lower cut off wavelength 270 nm. • Frequency doubling is almost equal to that of KDP.
L-alanine2-furoic acid(LA2FA) [35]	a=3.97Å,b =7.09Å, c=10.69, Triclinic, P1	• The material is stableupto122°C.The lowercut offfrequencywasaround245nm. • Third order non linear susceptibility value is 2.397 x 10^{-4}.
L-alaninium succinate [36]	Molecular structure confirmed by FTIR and FTNMR	• The lower cut off wavelength is 190 nm. • SHG efficiency is 23% higher than that of KDP
L- alanine tartrate (pure and lanthanam doped) [37]	Pure LAT: a = 5.790 Å, b = 6.386 Å, c = 12.157 Å, Lanthanam doped LAT: a = 5.823 Å, b = 6.372 Å, c = 12.121 Å, both are monoclinic system with P21 space group	• The lower cut-off wavelength of pure and doped crystals occurs at 246nm and 235nm, • SHG efficiency of pure and doped LAT crystals is nearly 1.18 and 1.40 times greater than KDP.
L-alanine potassium chloride [38]	a = 11.52746 Å, b = 15.70642 Å, c = 4.76734 Å, Triclinic	• The lower cut off wavelength is 193nm. The crystal is highly transparent to the wavelengths above 193nm to 1500nm
L-alanine potassium bromide [39]	a = 6.0867 Å, b = 12.5738 Å, c = 5.8713 Å, orthorhombic system and the space group is $P2_12_12_1$	• SHG efficiency is 3.22 times higher than that of KDP
L-alanine alaninium picrate (LAAP) [40]	a = 8.263(3) Å, b = 7.515(2) Å, c = 15.536(4) Å, monoclinic system with P21 space group	• SHG efficiency is 1.47 times higher than that of KDP
L - arginine maleate [41]	a=5.264 (3) Å, b=8.039 (3) Å, c=9.784 (3) Å, α=106.19 (3)°, β=97.24 (3)°, γ=101.66 (2)° & Triclinic, P1	• Thermal stability 221.5°C. Hardness value initially increases with applied load and then it decreases beyond the applied load of 7 g. • SHG efficiency is 1.4 times greater than that of KDP.
Copper doped L-arginine monohydrochloride monohydrate [42]	a= 11.049 Å, b=8.447 Å, c=11.212 Å, β=91.48 & monoclinic, $P2_1$	• Lower cut off wavelength 228 nm. • SHG efficiency is 59.3 % higher than that of KDP.
Glycine doped L-arginine monohydrochloride monohydrate [42]	a= 11.038 Å, b=8.469 Å, c=11.204 Å, β=91.30 & monoclinic, $P2_1$	• Lower cut off wavelength 228 nm. • SHG efficiency is 56.12% higher than that of KDP.
L-Arginine Acetate (LAA) [43]	s a= 9.221 Å, b = 5.184 Å and c = 13.090 Å, monoclinic system with space group $P2_1$	• Lower cut off wavelength of 240 nm.
L-arginine hydrochloride	a = 11.07 Å b = 8.50 Å c = 11.22 Å , monoclinic system	• L-arginine hydrochloride monohydrate single crystal SHG value was found to be 0.17 with

monohydrate [44]	with the space group P21	respect to Urea and 0.38 times that of KDP
L-arginine hydrochloride [45]	For hydrated LAHCL, a = 11.314 Å b = 8.298Å c = 11.054 Å , For anhydrous LAHCL, , a = 5.1937 Å b = 9.487Å c = 20.0235 Å monoclinic system with the space group P21	• Thermal stability 220°C. The intensity of green lightis more in the case of hydrated LAHCl crystal thanthat of anhydrous LAHCl crystal.
L-arginine phosphate (LAP) [46]	a = 10.85 Å b = 7,91 Å c = 7.32Å , monoclinic system with the space group P21	• LAP proposed as a replacement of KDP by chinese scientist.
L-Arginine Semicarbazone dihydrate [47]	a = 11.05 Å b = 8.49 Å c = 11.27Å , monoclinic system with the space group $P2_1$	• The lower cut off wavelength at around 350 nm. • The second harmonic generation is confirmed by the emission of green light and its efficiency is found to be 0.51 times that of KDP crystal.

6. Conclusion

In this article few of the L-alanine and arginine based NLO materials SHG efficiency discussed. These crystals have wide transparancy , considerable thermal stability and shows low dielectric loss at high frequency. These properties are the desirable one for the fabrication of opto electric and electro optic devices. So, These materials are suitable and potential candidate for Photonics industry.

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