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A Review on Physical and Chemical Properties of L-Phenylalanine Family of NLO Single Crystals

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Abstract: The semi organic nonlinear optic material has wide range of applications in opto electronic devices such as optical communication and optical storage devices. Amino acids are well suited to fulfill these requirements. In this review, family of L-phenylalanine complexes were analysed. By that, these complexes exhibit the properties such as NLO, thermal stability, negative photoconductivity and low dielectric loss make the material suitable for Opto electronics device fabrication.

1. Introduction

Recent advancement in making photonic devices rely on the non-linear optic materials. The interaction of electromagnetic waves with the atom causes the changes in polarizability of the dipole. This change causes the optical behavior as nonlinear. L-Phenyl alanine is one of the twenty amino acid which exhibit the non linear optical property. It has phenyl and in dole rings and it is classified as non-polar[1].Many number of natural amino acids are individually exhibiting the non linear optical properties because they are characterized by chiral carbons, a proton donating carboxyl (-COOH) group and the proton accepting amino($-NH_2$) group. The crystal structures of amino acids and their complexes have provided a wealth of interesting information to the patterns of their aggregation and the effect of other molecules and ions on their interactions and molecular properties[2]. Among them, L-phenylalanine is an essential protein amino acid, which is used by the body to build neurotransmitters. In this review we have consolidated the work on family of L-phenylalanine compounds which may provide enough assistance for the researchers, works on these compounds. Similar work for the family of L-Histidine was carried out [3].

2. Materials and Methods

In this review the crystals of L-Phenylalanine family are analysed. Slow evaporation solution growth technique is used to synthesis the crystals of L- Phenylalanine family. It is the most widely used method for the growth of single crystals, when the starting materials are unstable at high temperatures [4] and also which undergo phase transformations below melting point [5].

Materials having moderate to high solubility in temperature range, ambient to 100°C at atmospheric pressure can be grown by low-temperature solution method [6]. The mechanism of crystallization from solutions is governed, in addition to other factors, by the interaction of ions or molecules of the solute and the solvent which is based on the solubility of substance on the thermodynamical parameters of the process;

temperature, pressure and solvent concentration[7]. The advantages of low temperature crystal growth issimple and straight forward. Equipment design which gives a good degree of control of accuracy of ± 0.01 ºC. Due to the precise temperature control, super saturation can be very accurately controlled. Also efficient stirring of solutions reduces fluctuations to a minimum. The low temperature solution growth technique is well suited to those materials which suffer from decomposition in the melt or in the solid at high temperatures and which undergo structural transformations while cooling from the melting point. This advantage makes these compounds to be grown using this technique. The low temperature solution growth technique also allows variety of different morphologies and polymorphic forms of the same substance can be grown by variations of growth conditions or of solvent[8]. The proximity to ambient temperature reduces the possibility of major thermal shock to the crystal both during growth and removal from the apparatus. It is possible to grow large crystals of high perfections as the growth occurs close to equilibrium conditions [9].

3. L-Phenylalanine Family of NLO Single Crystals

Organic nonlinear optic materials has the facility that resonance due to conjugated bonds various Donor-acceptor substituents, possibility of inter and intra hydrogen bonds . Amino acids provides these advantages like crystallized in noncentrosymmetric space group, contain asymmetric carbon atom, contains deprotonated carboxylic acid group and protonated amino group[10],molecular chirality,absence of strongly conjugated bonds which leads to wide transparency ranges in the visible and UV spectral regions and zwitterionic nature of the molecule which is responsible for crystal hardness[11] . Hence much attention is devoted for semiorganic nonlinear optical material.

3.1 L-Phenylalanine hyrochloride (LPAHCL)

LPAHCl crystals were grown using slow evaporation technique [12]. The single crystal X-ray diffraction analysis reveals that the crystal belongs to orthorhombic crystal system with the space group $P2_12_12_1$ and the lattice parameters a = 27.762Å b=7.039 Å c=5.376 Å V= 1050 $Å^3$. The UV analysis reveals that cut off wavelength is around 350 nm. The thermal analysis shows that the crystal is thermally stable upto 229°C. The dielectric studies shows that the crystal has low value of dielectric loss. Optical absorptions study reveals that the optical band gap of the crystal is 3.7eV. The SHG efficiency is found to be 2 times of KDP. Photo conductivity measurements confirms negative photoconductivity, means that the dark current is more than photo current.

3.2 L-Phenylalanine L-Phenylalaninium nitrate (LPALPAN)

Single crystals of LPALPAN were grown using slow evaporation technique [13]. The single crystal X-ray diffraction analysis reveals that the crystal belongs to monoclinic crystal system with the space group $P2_1$and the lattice parameters a=12.53 Å b=5.375 Å c=14.96 Å V=959.89 $Å^3$. The UV analysis reveals that cut off wavelength is around 300 nm. The thermal analysis shows that the crystal is thermally stable upto 168°C. The dielectric studies shows that the crystal has low value of dielectric loss. The SHG efficiency is found to be 1.7 times of KDP. Photo conductivity measurements confirms the property of negative photoconductivity of the crystal.

3.3 L-Phenylalanine benzoic acid (LPABA)

Single crystals of LPABA were grown using slow evaporation technique [14]. The single crystal X-ray diffraction analysis reveals that the crystal belongs to monoclinic crystal system with the space group $P2_1$and the lattice parameters a=5.419 Å b=7.438 Å c=17.814 Å V=717.1 $Å^3$ β =92.94°. The UV analysis reveals that cut off wavelength is around 254nm. The thermal analysis shows that the crystal is thermally stable upto 134°C. The dielectric studies shows that the crystal has low value of dielectric loss. The SHG efficiency is found to be 1.6times of KDP. The microhardness test reveals that microhardness number decreases with increase in load.

3.4 L-Phenylalaninium maleate (LPAM)

Single crystals of LPAM were grown using slow evaporation technique[15]. The single crystal X-ray diffraction analysis reveals that the crystal belongs to monoclinic crystal system with the space group $P2_1$ and the lattice parameters a=11.057 Å b=5.330 Å c=11.472 Å V=679 $Å^3$ β = 101°. The UV analysis reveals that cut off wavelength is around 240nm. The thermal analysis shows that the crystal is thermally stable upto 127°C. The dielectric studies shows that the crystal has low value of dielectric loss. Optical absorptions study reveals that the optical band gap of the cystal is 4.85eV.The SHG efficiency is found to be 1.7 times of KDP. Photo conductivity measurements confirms the property of negative photoconductivity of the crystal.

3.5 L-Phenylalanine L-Phenylalaninium per chlorate(LPALPAPC)

Single crystals of LPALPAPC were grown using slow evaporation technique [16]. The single crystal X-ray diffraction analysis reveals that the crystal belongs to orthorhombic crystal system with the space group $P2_12_12_1$and the lattice parameters a=5.39 Å b=12.683 Å c=29.157 Å V=1993.21Å^3. The UV analysis reveals that cut off wavelength is around 310nm. The thermal analysis shows that the crystal is thermally stable upto 206°C.

The dielectric studies shows that the crystal has low value of dielectric loss. The SHG efficiency is found to be 1.4 times of KDP. The microhardness test reveals that microhardness number decreases with increase in load. Photo conductivity measurements confirms the property of negative photoconductivity of the crystal.

3.6 L-Phenylalanine L-Phenylalaninium dihydrogen phosphate (LPLPADHP)

Single crystals of LPLPADHP were grown using slow evaporation technique [17]. The single crystal X-ray diffraction analysis reveals that the crystal belongs to monoclinic crystal system with the space group $P2_1$and the lattice parameters a=13.4408 Å b=4.8762 Å c=15.4707 Å V=1005.99 Å^3 β = 97°. The UV analysis reveals that cut off wavelength is around 330nm. The thermal analysis shows that the crystal is thermally stable upto 161°C. The dielectric studies shows that the crystal has low value of dielectric loss. Optical absorption study reveals that the optical band gap of the cystal is 4.29eV.The SHG efficiency is found to be 1.2 times of KDP. The microhardness test reveals that microhardness number decreases with increase in load.

3.7 L-Phenylalanine-4-Nitrophenol (LPANP)

L-Phenylalanine-4-nitrophenol crystals were grown using slow evaporation technique [18], [19]. The single crystal X-ray diffraction analysis reveals that the crystal belongs to monoclinic crystal system with the space group $P2_1$and the lattice parameters a=5.84 Å, b=7.01Å, c=17.87Å,V=728.32 Å^3. The UV analysis reveals that cut off wavelength is around 320nm.The thermal analysis shows that the crystal is thermally stable upto 165°C. The dielectric studies shows that the crystal has low value of dielectric loss. The SHG efficiency is found to be 1.2 times of KDP. TheVicker's microhardness test reveals that microhardness number decreases with increase in load. Photo conductivity measurements confirms the property of negative photoconductivity of the crystal.

3.8 L-Phenylalanine fumaric acid (LPFA)

L-Phenylalanine fumaric acid crystals were grown using slow evaporation technique [20]. The single crystal X-ray diffraction analysis reveals that the crystal belongs to triclinic crystal system with the space group P1and the lattice parameters a=5.78 Å ,b=11.64 Å, c=11.67 Å,V=712 Å^3,α=68.22°,β=80.60°,γ=79.14°.The UV analysis reveals that cut off wavelength is around 240 nm. The thermal analysis shows that the crystal is thermally stable upto 208°C. The SHG efficiency is found to be similar of KDP.

3.9 L-Phenylalanine trichloro acetate (LPTCA)

L-Phenylalanine trichloro acetate crystals were grown using slow evaporation technique [21]. The single crystal X-ray diffraction analysis reveals that the crystal belongs to monoclinic crystal system with the space groupP21and the lattice parameters a=19.68 Å, b=6.11 Å, c=27.26 Å,V=3013Å^3,β=113.27°.The UV analysis reveals that cut off wavelength is around 254 nm.The thermal analysis shows that the crystal is thermally stable upto 136°C. Optical absorption study reveals that the optical band gap of the cystal is 4.89eV. The SHG efficiency is found to be 0.65 times of KDP.

3.10 L-Phenylalanine L-phenylalaninium malonate (LPLPAM)

L-Phenylalanine L-Phenylalaninium malonate crystals were grown using slow evaporation technique by prakash et al [22]. The single crystal X-ray diffraction analysis reveals that the crystal belongs to monoclinic crystal system with the space group $P2_1$and the lattice parameters a=14.021 Å, b=5.5077 Å, c=14.597 Å,V=1075.2 $Å^3$,β=107.39°. The UV analysis reveals that cut off wavelength is around 233 nm. The thermal analysis shows that the crystal is thermally stable upto180°C. The dielectric studies shows that the crystal has low value of dielectric loss. The SHG efficiency is found to be 0.38 times of KDP.

3.11 L-Phenylalanine nitric acid (LPN)

L-Phenylalanine nitric acid crystals were grown using slow evaporation technique [23]. The single crystal X-ray diffraction analysis reveals that the crystal belongs to monoclinic crystal system with the space group $P2_1$and the lattice parameters a=12.49 Å b=5.39 Å c=14.91 Å V=947 $Å^3$ β=108°. The UV analysis reveals that cut off wavelength is around 300 nm. The thermal analysis shows that the crystal is thermally stable upto 205°C. The dielectric studies shows that the crystal has low value of dielectric loss. The SHG efficiency is found to be 0.26 times of KDP.

4. Results and Discussion

The growth of crystals from aqueous solution, which is one of the most popular technique in the production of technically important crystals, especially to grow NLO crystals. This paper summarizes some of the physical properties such as lattice parameters, Second harmonic generation parameter, thermal stability, UV optical cut off wavelength, photo conductivity, micro hardness and band gap energy in the application point of view and are listed in Table 1.

Table 1. Important properties of L-Phenylalanine crystals

NAME OF THE COMPOUND	SINGLE CRYSTAL PARAMETER	SHG PARAMETER	THERMAL STABILITY	UV OPTICAL CUT OFF	PHOTO CONDUCTIVITY	MICRO HARDNESS	BAND GAP ENERGY
L-Phenylalanine Hydrochloride $C_9H_{12}NO_2Cl$	a = 27.762Å b=7.039 Å c=5.376 Å V= 1050 $Å^3$ Orthorhombic $P2_12_12_1$	2 times greater than KDP	Stable up to 229°C	350nm	Negative photo conductivity (Dark current is more than photo current)		3.7eV
L-Phenylalanine L-Phenylalaninium nitrate $C_9H_{11}NO_2.C_9H_{12}NO_2H^+.NO_3^-$	a=12.53 Å b=5.375 Å c=14.96 Å V=959.89 $Å^3$ Monoclinic $P2_1$	1.7 times of KDP	Stable up to 168°C	300nm	Negative photo conductivity		
1 1 1 L-Phenylalanine Benzoic acid $C_9H_{11}NO_2.C_7H_6O_2$	a=5.419 Å b=7.438 Å c=17.814 Å V=717.1 $Å^3$ β =92.94° Monoclinic $P2_1$	1.6 times of KDP	Stable upto 134°C	254nm	Negative photo conductivity	Micro hardness number decreases with increase in load (Hard materials)	
L- Phenylalaninium maleate $C_6H_5CH_2CH(NH_3)^+COOH.C_4H_3O4$	a=11.057 Å b=5.330 Å c=11.472 Å V=679 $Å^3$ β = 101° Monoclinic $P2_1$	1.5 times of KDP	Stable upto 127°C	240nm	Negative photo conductivity		4.85eV
L-Phenylalanine L-Phenylalaninium per chlorate $C_9H_{11}NO_2C_9H_{12}NO_2^+.ClO_4^-$	a=5.39 Å b=12.683 Å c=29.157 Å V=1993.21$Å^3$ Orthorhombic P2 2 2	1.4 times of KDP	Stable upto 206°C	310nm	Negative photo conductivity	Micro hardness number decreases with increase in load (Hard materials)	
L-Phenylalanine L-Phenylalaninium dihydrogen phosphate $C_9H_{11}NO_2.C_9H_{12}NO_2^+.H_2PO_4^-$	a=13.4408 Å b=4.8762 Å c=15.4707 Å V=1005.99 $Å^3$ β = 97° Monoclinic $P2_1$	1.2 times of KDP	Stable upto 161°C	330nm		Micro hardness number decreases with increase in load (Hard materials)	4.29eV

L-Phenylalanine-4-Nitrophenol	a=5.84 Å b=7.01 Å c=17.87 Å V=728.32 $Å^3$ Monoclinic $P2_1$	1.2 times of KDP	Stable upto 165°C	320nm	Negative photo conductivity	Micro hardness number increases with increase in load (Soft materials)	3.87eV
L-Phenylalanine Fumaric acid $C_9H_{11}NO_2$	a=5.78 Å b=11.64 Å c=11.67 Å V=712A3 Å α =68.22° β=80.60° γ=79.14° Triclinic P_1	Similar to KDP	Stable upto its melting point 208°C	240nm			
L- Phenylalaninium trichloroacetate $C_9H_{12}NO_2^+.C_2Cl_3O_2^-.H_2O$	a=19.68 Å b=6.11 Å c=27.26 Å V=3013 $Å^3$ β=113.27° Monoclinic $P2_1$	0.65 times of KDP	Stable upto 136°C	254nm			4.89eV
L-Phenylalanine L-Phenylalaninium malonate $C_9H_{11}NO_2.C_9H_{12}NO_2^+.C_3H_3O_4^-$	a=14.021 Å b=5.5077 Å c=14.597 $Å^3$ V=1075.2 Å β=107.39° Monoclinic $P2_1$	0.38 times of KDP	Stable upto to 180°C	300nm			
L-Phenylalanine nitic acid $C_9H_{11}NO_2H^+ NO_3^-$	a=12.49 Å b=5.39 Å c=14.91 Å V=947 $Å^3$ β=108° Monoclinic $P2_1$	0.26 times of KDP	Stable upto 205°C	295nm			

L-Phenylalanine family of NLO crystals are found to be semiorganic and its properties excel with NLO efficiency, thermal stability, photo negativity and microhardness. Due to its excellent properties it has a very wide applications in photonics as well as optoelectronics.

Conclusion

This review dealt with Non linear optical L-phenylalanine family of single crystal. These crystals were grown by slow evaporation technique. From the results it is very clear single crystals of L-phenylalanine family can be used as promising material for NLO and photonic device applications. This review will provide useful knowledge for the researchers to continue their research with various compounds to achieve a highly NLO potential crystal.

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