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Growth and characterization of L-phenylalanine nitric acid (LPN) and tris L-(phenylalanine)-phenylalanininum nitrate (TPLPN) as second and third order nonlinear optical materials

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ABSTRACT

We synthesized noncentrosymmetric single crystals of L-phenylalanine nitrate (LPN) and tris L-(phenylalanine) L-phenylalaninium nitrate (TPLPN) by slow solvent evaporation technique. Both crystallized in monoclinic system with different acentric space groups namely $P2_1$ (LPN) and C2 (TPLPN) respectively. The IR and Raman spectral investigation was done for LPN and TPLPN and discussed. The UV-vis-studies accomplished the excitation wavelength of the grown crystals suitable to exhibit second harmonic generation signal. From the absorption data, remarkable optical properties such as direct band gap energy, Urbach energy, extinction coefficient were evaluated. The mechanical strength of the grown crystal was examined by Vickers micro hardness test. The temperature of decomposition was confirmed by TG/DSC analysis. Fluorescence emission spectrum of LPN and TPLPN were recorded and lifetime was also studied. The dielectric constant and dielectric loss of LPN and TPLPN has been determined as a function of frequency and temperature. Also the surface topologies of the crystallized salts were assessed by SEM studies. The third-order nonlinearities of LPN and TPLPN were determined by Z-scan technique with Nd: YAG at 532 nm and thereby from closed and open Z-scan data, third-order susceptibilities were calculated to be $\chi^{(3)} = 8.826 \times 10^{-6}$ esu for LPN and $\chi^{(3)} = 2.552 \times 10^{-7}$ esu for TPLPN.

1. Introduction

Due to the increasing demand of nonlinear optical (NLO) crystals in recent years, researchers have been concentrating on amino acids possessing π-conjugated electrons showing remarkably attractive second and third-order optical nonlinearities. The nonlinear optical effect usually refers to such as secondary (or) higher effect of the magnitude of an applied electric field by causing an electric polarizing response in a substance, proportional to the magnitude of the strong applied laser beam. Nonlinear optical phenomena have received a tremendous interest after the advent of lasers sources and occupies a key position in the development of laser technology [1]. The applications of organic NLO crystals are very much realized in hi-tech lasers than the inorganic counterparts and also enhancement of physico-chemical properties were discovered by increasing the intermolecular interactions [2] which steered to

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numerous design possibilities. The characteristics of aminoacids based organic materials are indeed more attractive in regard to their polarization behaviour and asymmetrical crystal structures which encourage their use in high optical data storage, color displays and fibre optical communications with improved performance. The wider choice of third order nonlinear materials have superiority of high nonlinearity, low transformation temperature, fast response and high transparency, constitute to possess more demanding than any other system [3]. In particular, the strong delocalization of π-electron root to large nonlinear susceptibility and molecular hyperpolarizability in the organic molecule could lead to significant enhancement of the third-order nonlinear optical properties of the materials [4].These characteristics of organic materials promote their use in photonic and optoelectronic switching devices which forms the basis for future optical systems. Many important proteinogenic and nonproteinogenic amino acids also play censorious non protein roles within the body. Among the aminoacid groups, L-phenylalanine is used as a precursor by brain to produce nor-epinephrine and dopamine that transmit signals between nerve cells and the brain thereby helps in adequate improvement of memory [5]. In literature L-phenylalanine based organic asymmetric crystals have been studied and manifested as suitable nonlinear optical materials [6–10]. An aromatic and hydrophobic amino acid L-phenylalanine mixed with nitric acid in different stoichiometric ratios (2:1 and 4:1) has been already synthesized and reported in literature [11,12]. Recently L-phenylalanine dl-mandelic acid single crystal was communicated by Jayaprakash et al [13]. Herein we carried out the growth of LPN and TPLPN single crystals by slow evaporation technique to extend our work to study the triple effect of the wavelength of light in laser, that finds great important in science and technology including enhanced applications in the optoelectronic field owing to high demand for improving data rates in future optical communication techniques. Herewith we also carried out optical constant determination, fluorescence, lifetime measurement, microhardness and dielectric studies for the first time. The third harmonic studies by Z-scan technique on asymmetric compounds LPN and TPLPN was accomplished and reported, thus confirms their suitability as good nonlinear optical materials.

2. Experimental

2.1. Materials synthesis and crystal growth

As the initial reagents, we used L-phenylalanine (Lobo Chem) and nitric acid (SRL) to synthesize LPN and TPLPN in different stoichiometric ratios (2:1 and 4:1).The calculated amount of the L-phenylalanine and nitric acid in the respective ratios were mixed in solvents of deionized water and methanol. After stirring individually using a magnetic stirrer for 5 hours yielded homogenous saturated solutions. The solutions were then filtered and kept undisturbed in petry dishes for slow evaporation to take place at room temperature. We harvested optically transparent crystals of LPN and TPLPN crystallized in a span of 3 weeks. The photograph of single crystals of LPN and TPLPN are presented in Fig. 1(a) and (b).

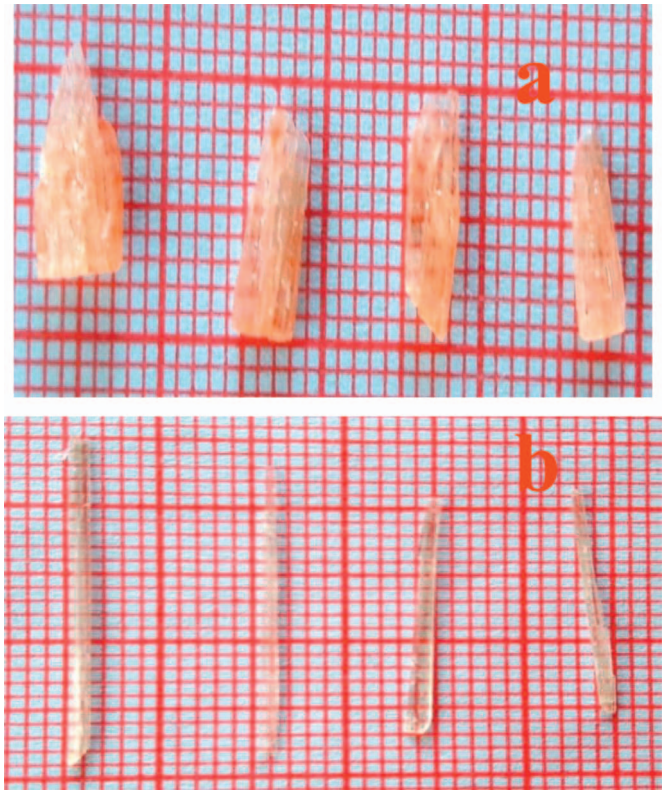

Fig. 1. (a) and (b). Photograph of single crystals of LPN and TPLPN.