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Growth, structural, optical and mechanical studies on Amino acids doped nonlinear optical sodium acid phthalate single crystals

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The slow evaporation technique was used to successfully grown amino acid doped sodium acid phthalate (NaAP) crystals at room temperature. A great deal of research has been done on the effects of amino acids on NaAP growth and characteristics. X-ray diffraction was used to examine the crystal structure and lattice parameters of the grown crystals. Functional groups were found in the title crystals, which revealed themselves utilizing FTIR spectra. The optical transparency of the doped crystals was noticed by measurements of optical absorption. In order to assess the mechanical strength of the produced crystals, Vickers microhardness tests were employed. The technique of Kurtz powder was utilized to calculate the second harmonic generation (SHG) performance of the cultivated crystals.

Keywords: Nonlinear optical material; FTIR; Micro hardness.

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Introduction

Nonlinear optical materials have fascinated researchers in photonics, lasers, electro-optic switches, and frequency conversion industries [1-11]. There have been many nonlinear materials synthesized in the last decade that include both organic and inorganic compounds. Although they had to overcome problems related to a low laser damage threshold, inadequate optical transmittance, and poor optical precision, their system applications have been hindered by these problems [12]. Because of the hydrogen bonding, pure organic crystals have lower mechanical robustness. Inorganic Nonlinear organic (NLO) materials have outstanding mechanical and thermal properties, but due to the lack of electron delocalization, they have only modest optical susceptibilities. [13-16]. Crystals from the Phthalic acid family are possible NLO materials that have a broad range of applications [17]. SHG applications benefit greatly from sodium acid phthalate [18, 19]. Slow evaporation was used to try to develop amino acids (L-alanine, L-arginine, and Glycine) doped sodium acid phthalate in this study. Because of the impact of doping on intrinsic defects, the effect of dopants is important [20-25]. The reports and characterization suggest that dopants strengthen optical, mechanical, and other properties.

I. Experiment

1.1. Crystal growth

1 mole %, 3 mole %, and 5 mole % of (AR grade) L-alanine, L-arginine, and glycine doped with pure sodium acid phthalate in double distilled water at ambient temperature for 5 hrs resulted in amino acids doped NaAP single crystals. A range of recrystallization processes was used to extract the impurities. The supersaturated solutions were filtered through a Whatmann filter and stored in a dust-free environment. Slow evaporation is required for all nine concentrations. Within 22, 20, and 21 days, L-alanine, L-arginine, and glycine doped NaAP crystals with different mole concentrations (1%, 3%, and 5%) were collected. Figures 1-3 display images of all doped NaAP crystals.

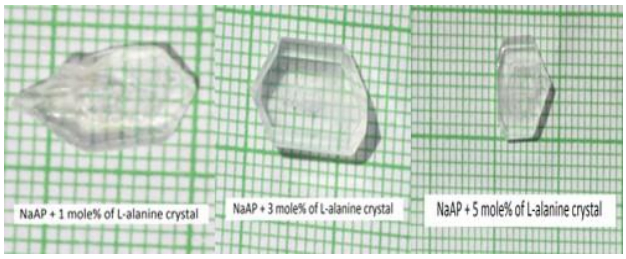

Fig. 1. Photograph of L-alanine doped NaAP crystals.

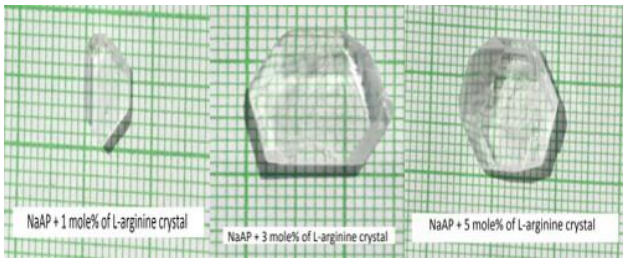

Fig. 2. Photograph of L-arginine doped NaAP crystals.

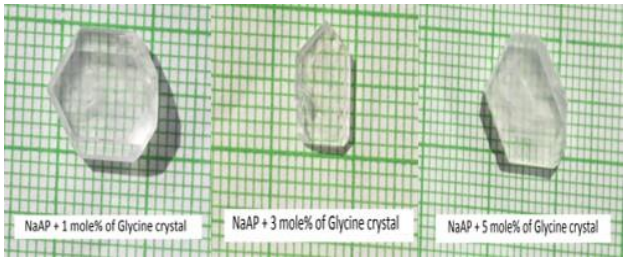

Fig. 3. Photograph of Glycine doped NaAP crystals.

II. Characterization studies

2.1. Single crystal X-ray diffraction analysis

To analyze the amino acids doped with sodium acid phthalate crystals, a single crystal X-ray diffractometer, the ENRAF NONIUS CAD4, was employed. Lattice parameters that have been computed are shown in table 1. The orthorhombic crystal system is in agreement with the literature, which states that all of the formed crystals belong to this system [18, 19].

2.2. FTIR analysis

In the study of doped NaAP single crystals, FTIR spectroscopy was utilized to prove the presence of functional groups and vibrational frequencies. Figures 4-6 display the spectra of the formed crystals, which were recorded using a Perkin-Elmer spectrum between 400 and 4000 cm^{-1}. When the aromatic ring is distorted out of the plane, a specific absorption band (namely, 538-858 cm^{-1}) is created. This band results from the aromatic ring's C-H in-plane deformation, which takes place at a wavelength of 1118 cm^{-1}. C-O stretching vibrations peaked at 1354 cm^{-1}. The peak centered at 1613 cm^{-1} is caused by the skeletal-aromatic vibrations of the ring.

Table 1.

Lattice parameters for pure and doped NaAP crystals.

Crystals	Unit cell parameters	Volume
NaAP (pure) [18]	a = 6.60 Å, b = 9.08 Å, c = 25.84 Å, α = β = γ = 90°	V = 1548 Å^3
NaAP + 1 mole% L-Alanine	a = 6.73 Å, b = 9.24 Å, c = 26.25 Å, α = β = γ = 90°	V = 1631 Å^3
NaAP + 3 mole% L-Alanine	a = 6.74 Å, b = 9.23 Å, c = 26.28 Å, α = β = γ = 90°	V = 1635 Å^3
NaAP + 5 mole% L-Alanine	a = 6.77 Å, b = 9.28 Å, c = 26.35 Å, α = β = γ = 90°	V = 1655 Å^3
NaAP + 1 mole% L-Arginine	a = 6.78 Å, b = 9.29 Å, c = 26.38 Å, α = β = γ = 90°	V = 1661 Å^3
NaAP + 3 mole% L-Arginine	a = 6.77 Å, b = 9.30 Å, c = 26.39 Å, α = β = γ = 90°	V = 1662 Å^3
NaAP + 5 mole% L-Arginine	a = 6.87 Å, b = 9.45 Å, c = 26.76 Å, α = β = γ = 90°	V = 1737 Å^3
NaAP + 1 mole% Glycine	a = 6.68 Å, b = 9.19 Å, c = 26.06 Å, α = β = γ = 90°	V = 1600 Å^3
NaAP + 3 mole% Glycine	a = 6.74 Å, b = 9.28 Å, c = 26.29 Å, α = β = γ = 90°	V = 1644 Å^3
NaAP + 5 mole% Glycine	a = 6.81 Å, b = 9.38 Å, c = 26.62 Å, α = β = γ = 90°	V = 1701 Å^3

1696 cm^{-1} is the vibration frequency of the C=O bond vibrations in the carboxyl group. The values recorded for NaAP crystals were perfectly represented by all of these assignments [18].

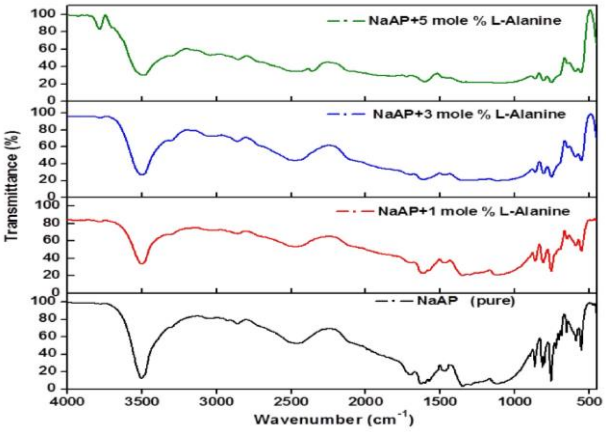

Fig. 4. FTIR Spectra of pure and L-Alanine doped NaAP crystals.

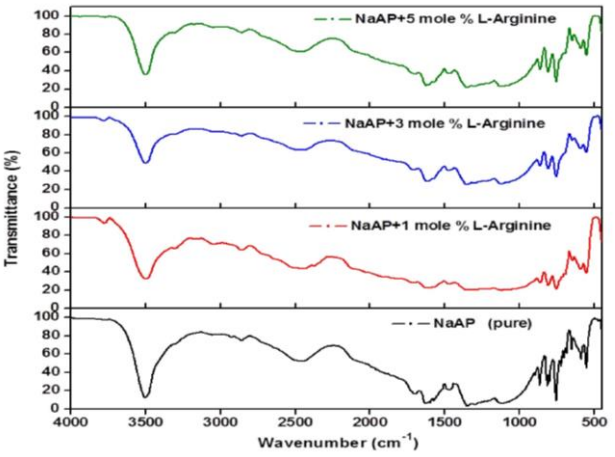

Fig. 5. FTIR spectra of pure and L-Arginine doped NaAP crystals.

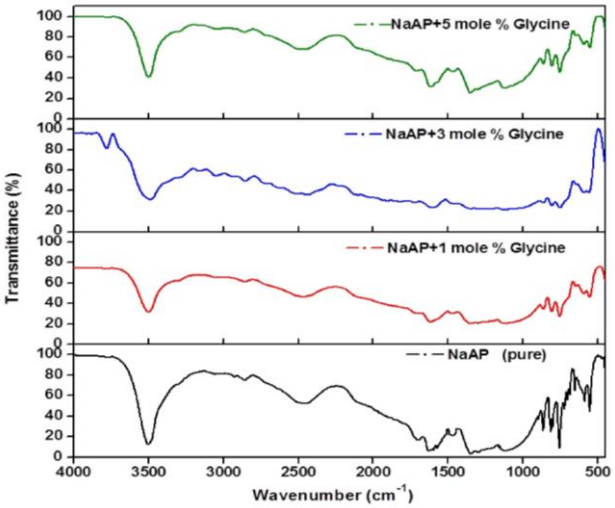

Fig. 6. FTIR spectra of pure and Glycine doped NaAP crystals.

The NH_3^+ asymmetric stretching mode assigned to L-alanine dopants was 2867 cm^{-1}, and the deprotonated carboxylic group (COO^-) characteristic absorption band was 1468 cm^{-1}. The NH_2 asymmetric stretching vibrational mode peaks at 3501 cm^{-1}, C-H stretching of CH_2 vibrations assigned at 2468 cm^{-1}, and the NH_2 symmetric bending mode peaks is found to be at 1466 cm^{-1}. The NH_3^+ rocking mode for out plane bending was observed at 1125 cm^{-1}, and the C-O symmetric stretching vibrational mode at 1467 cm^{-1}. Glycine dopants were detected at 3161 cm^{-1}, due to the NH_3^+ asymmetric stretching vibrational mode, and 1467 cm^{-1} for the C-O symmetric stretching vibrational mode. Following the procedures described above, it was verified that amino acids are used as dopants in NaAP single crystals.

2.3. UV-Vis-NIR spectral analysis

An ultraviolet-visible-near infrared spectrophotometer (Perkin Elmer Lambda 35) was used for the spectral analysis with a range of 300-800 nm. The obtained spectra are presented in Figure 7. UV cut-off wavelengths of 313, 320, and 317 nm were found for L-alanine, L-arginine, and glycine-doped NaAP crystals, respectively. The absorbance also falls when the doping concentration increases for each of the three dopants. The presence of dopants enhances the material's optical characteristics in this example. Additionally, this lack of absorption in the visible area suggests the appropriateness for processing optoelectronic devices. In order to calculate the optical absorption coefficient (α), the following relationship was used;

$$\alpha = \frac{1}{t}\log\left(\frac{1}{T}\right). \qquad (1)$$

Where, T is the transmittance and t is the crystal thickness. For high photon energies (hυ), the crystal's absorption coefficient (α) consisted mainly of the following equation;

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu}. \qquad (2)$$

In this equation, E_g is the optical bandgap of the crystal and A is a constant. Figure 8 plots the variation of $(\alpha h\nu)^2$ vs. (hν) and the bandgap for pure NaAP crystals is calculated as 4.050 eV using the linear component of the accessible for concentrations of alanine doped NaAP, the bandgap values are 4.07eV; and, for concentrations of alanine doped NaAP between 3 mole% and 5 mole%, the bandgap values are 4.075 and 4.077 eV. E_g is determined to be 4.048, 4.051, and 4.052 eV for arginine doped NaAP, and 4.054, 4.063, and 4.066 eV for glycine-doped NaAP when the respective mole concentrations are 1 mole, 3 mole, and 5 mole%.

2.4. Microhardness measurements

Vickers microhardness testing on the title crystals was carried out using a Wetzler diamond indenter. A load of 25-100 g was applied to the plane of pure and doped NaAP crystals, and the resulting indentation was measured. The indentation time was 25 seconds for both attempts. To obtain the Vickers hardness number, the

formula given below was used;

$$H_v = 1.8544\ (P/d^2)\quad kg/mm^2 \qquad (3)$$

The value P applied in kilograms is the product of d, the indentation of the impression's diagonal length in mm^2. The following figure 9 illustrates the modification of H_v with applied load P. The microhardness increases

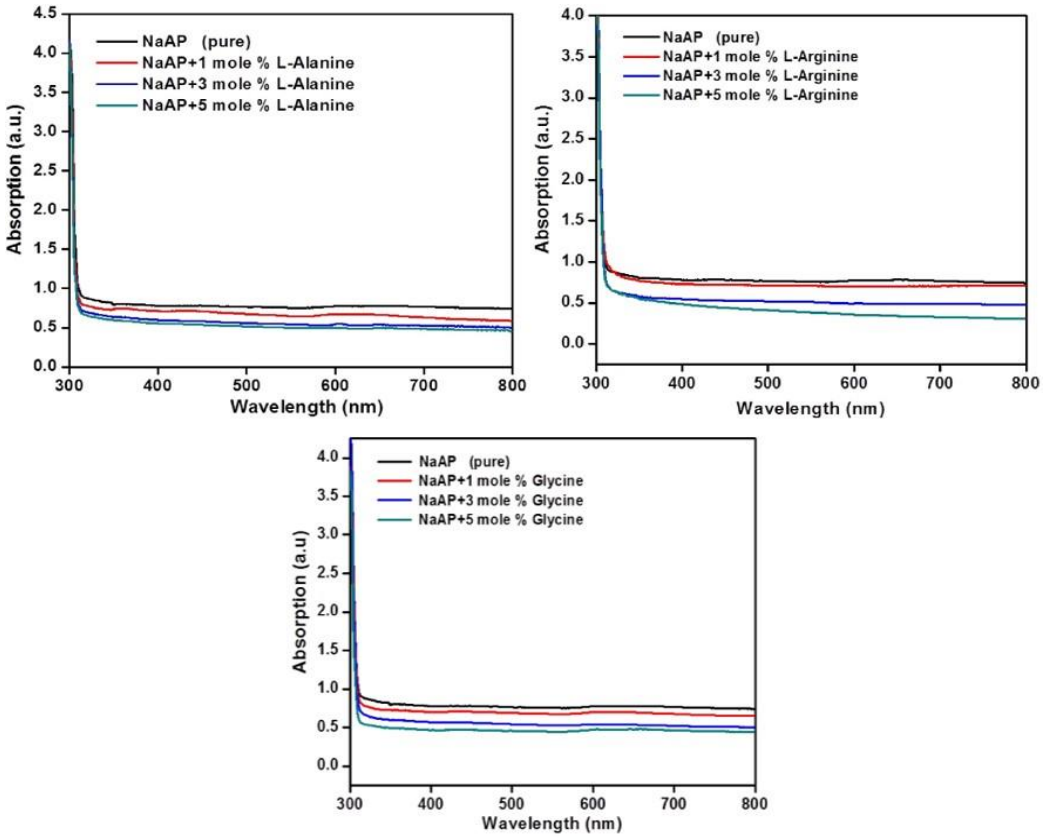

Fig. 7. Optical absorption spectra of pure and doped NaAP crystals.

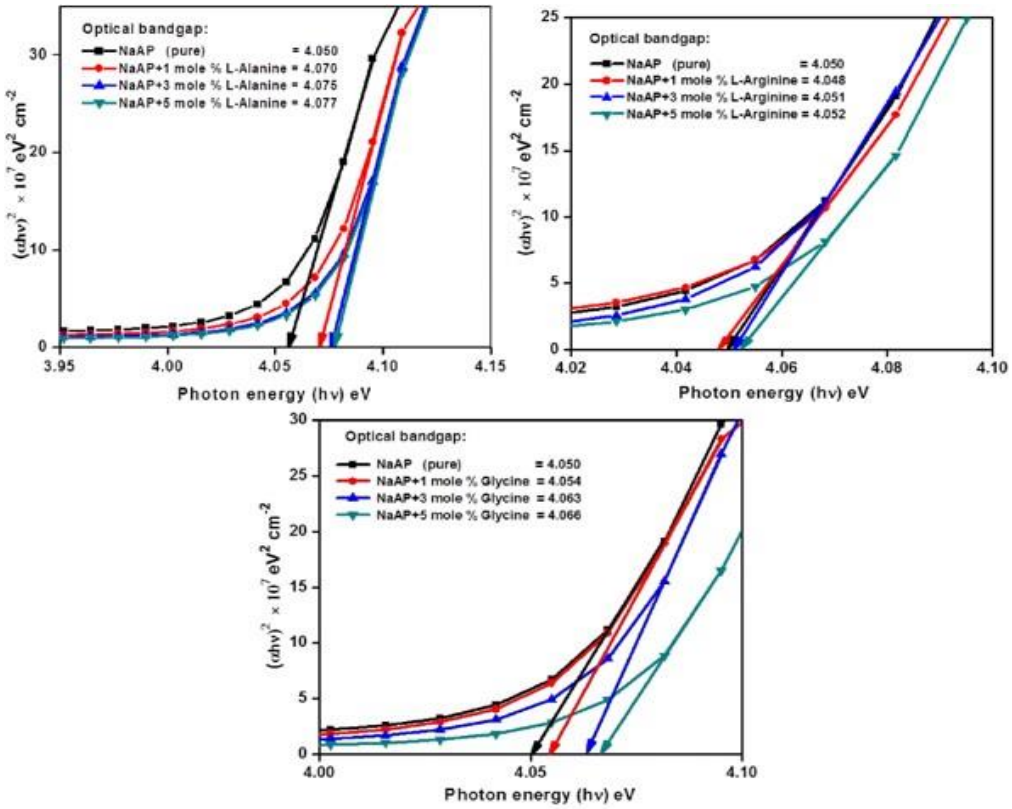

Fig.8. Plot of $(\alpha h\nu)^2$ vs. $(h\nu)$.

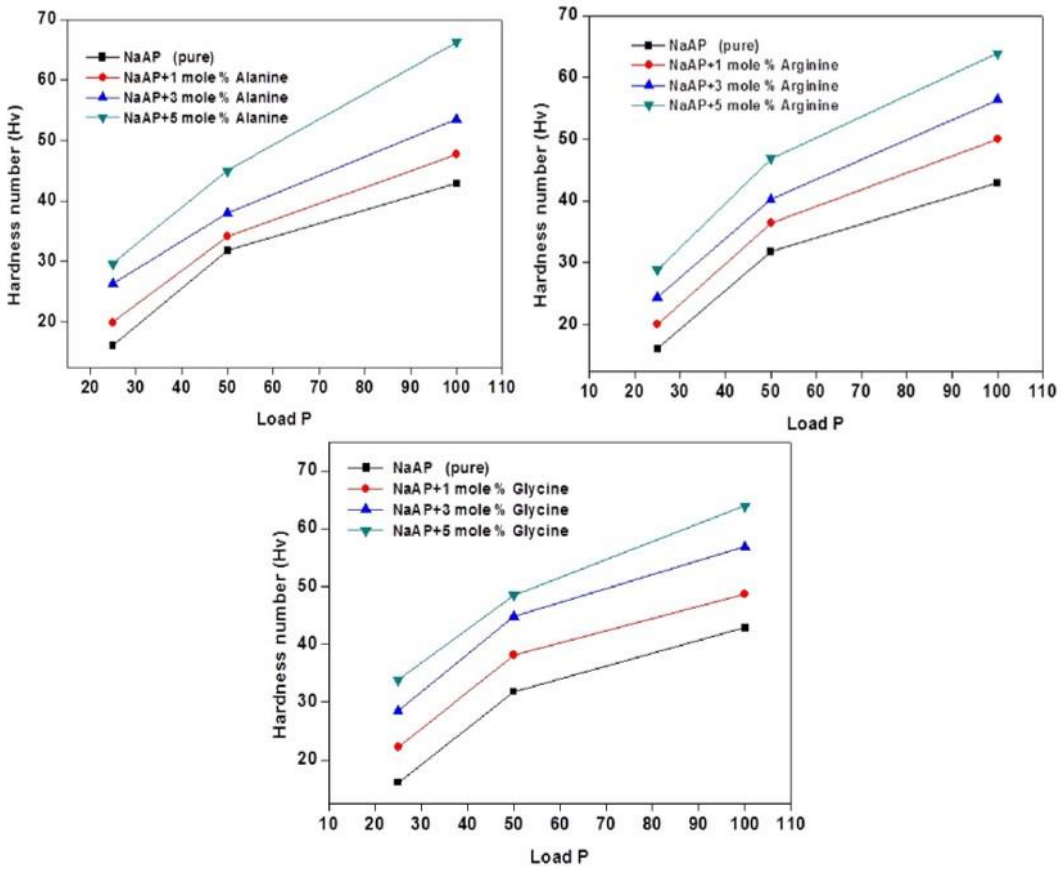

Fig. 9. Plot of Load P vs. H_V.

continuously when the mole percentage of L-alanine doped NaAP crystals is raised. Results were consistent across different L-arginine and glycine-doped NaAP crystal mole percentages. Since the presence of dopants improve the material's hardness.

2.5. Nonlinear Optical studies

NLO study was conducted to assess the SHG efficiency of sodium acid phthalate single crystals utilizing the Kurtz powder test employing a Q-switched Nd:YAG laser. The infrared light beam passed on powder samples of amino acids doped NaAP crystals with a fundamental wavelength of 1064 nm, a pulse intensity of 850 mJ per second, pulse duration of 9 ns, and a repetition rate of 10 Hz. A less efficient SHG (than the KDP crystal) is found in the doped crystal. The SHG efficiency can be estimated by discussing the data in table 2.

Table 2.

SHG efficiency of Doped NaAP crystals.

Crystals	SHG efficiency
KDP (pure)	1.00
NaAP (pure) [18]	1.57
NaAP + 1mole% L-Alanine	0.886
NaAP + 3 mole % L-Alanine	0.750
NaAP + 5 mole % L-Alanine	0.556
NaAP + 1 mole % L-Arginine	0.488
NaAP + 3 mole % L-Arginine	0.660
NaAP + 5 mole % L-Arginine	0.704
NaAP + 1 mole % Glycine	0.715
NaAP + 3 mole % Glycine	0.772
NaAP + 5 mole % Glycine	0.806

Conclusions

The slow evaporation solution growth method was used to grown a single crystals of amino acids in the presence of sodium acid phthalate. Based on single crystal X-ray diffraction investigation, the title crystals confirm to the orthorhombic structure of the space group B2ab. FTIR spectroscopy was employed to design the current dopants for the Alkali metal-carboxylic acid group. The optical absorption spectra show that the amino acid dopants strengthened the material's optical properties. The mechanical hardness analysis shows that as the doping concentration increases, the hardness increases as well. According to the investigation, the SHG crystals have a lesser efficiency than the KDP crystal. All of this evidence suggests that the amino acid doped NaAP crystal could be a promising tool for optoelectronic device fabrication.

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Вирощування, структурні, оптичні та механічні дослідження легованих амінокислотами нелінійних оптичних монокристалів фталату натрію

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Для вирощування кристалів фталату натрію, легованого амінокислотами (NaAP) при кімнатній температурі, використано метод повільного випаровування. Досліджено вплив амінокислот на ріст і характеристики NaAP. Для дослідження кристалічної структури та параметрів решітки вирощених кристалів використано рентгенівську дифракцію. В кристалах, які виявили себе за допомогою FTIR спектрів знайдено функціональні групи. Оптичну прозорість легованих кристалів спостерігали за вимірюванням оптичного поглинання. Для оцінки механічної міцності отриманих кристалів використано дослідження мікротвердості за Віккерсом. Порошкова методика Курца використовувалася для розрахунку продуктивності генерації другої гармоніки (ГГГ) вирощених кристалів.

Ключові слова: нелінійні оптичні матеріали; FTIR; мікротвердість.