JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

SYNTHESIS AND NON-LINEAR OPTICAL STUDY OF POTASSIUM IODIDE INFLUENCED L-ASPARAGINES MONOHYDRATE CRYSTAL

[1]Mr. Rushikesh Bahire, [2]Dr. Jyoti Shegokar
[1]Assistant Professor, [2]Assistant Professor
[1]Department of Physics, [2]Department of Chemistry
College of Engineering & Technology, Akola, Maharashtra, India.

ABSTRACT

A semi-organic nonlinear optical crystal, L-Asparagine Potassium Iodide (LAMPI), was grown successfully using a simple solution-growth method with slow evaporation at room temperature. The crystal structure and quality were verified through powder X-ray diffraction analysis. Optical behaviour was examined using UV–Vis–NIR spectroscopy across the 200–1000 nm range, from which the transmission cut-off and band-gap energy of the LAMPI crystal were determined.

Keywords: LAMPI crystal, nonlinear optical materials, slow-evaporation growth, XRD analysis, UV–Vis spectroscopy.

INTRODUCTION

Nonlinear optics is increasingly important in modern photonic and optoelectronic technologies [1]. Organic nonlinear optical (NLO) materials are attracting significant interest due to their roles in optical communication, laser imaging, data processing, and protective photonic systems [2]. These materials often provide higher nonlinear response and lower fabrication cost compared to many inorganic crystals. Among organic systems, α-amino acids are notable for their chirality, hydrogen-bonding networks, broad transparency, and zwitterionic nature, which contribute to good optical and mechanical behaviour [4].

Amino-acid-based crystals are especially promising for NLO applications because their molecular structure allows hydrogen-bond formation and property tuning through chemical modification. L-Asparagine monohydrate (LAM), with formula $C_4H_8O_3N_2 \cdot H_2O$, crystallizes in the orthorhombic system and is stabilized by a network of hydrogen bonds [1–2]. Several related compounds—including LALT, LASP, and LAN have already been explored for nonlinear optical performance.

In this study, a semi-organic crystal grown from L-Asparagine monohydrate and potassium iodide was prepared and examined. The material was characterized using XRD, PXRD, UV–Vis–NIR, FT-IR, fluorescence, ^{1}H-NMR, microhardness, and NLO measurements, as semi-organic compounds continue to attract interest for their high nonlinearity and strong resistance to laser-induced damage [3].

Nonlinear optics (NLO) studies the behaviour of light in materials where the dielectric polarization (P) responds nonlinearly to the electric field (E). Efficient NLO crystals for the visible and UV regions are crucial for laser applications [5]. The first observation of nonlinear effects was made by Franken et al., who generated light at twice the frequency of a ruby laser using quartz [6]. In such materials, interacting photons can produce new photons with double the energy and half the wavelength. NLO crystals are widely used in optical information processing, data storage, frequency conversion, and telecommunications [7]. Amino acid salts, in particular, exhibit strong NLO properties [10]. Organic NLO crystals offer high nonlinear coefficients [9], inorganic crystals provide thermal and mechanical stability, and semi-organic crystals combine metals with organic ligands, offering tunable optoelectronic properties and environmental stability [8].

The semi-organic crystal **L-Asparagine Monohydrate Potassium Iodide (LAMPI)** was grown by slow evaporation. It crystallizes in an orthorhombic system with lattice parameters: a = 5.704 Å, b = 9.851 Å, c = 11.982 Å, volume V = 658.8 Å^3, and space group P212121. LAMPI's structure features a network of hydrogen bonds between asparagine molecules and water, contributing to its stability.

A **single crystal** is a material in which the crystal lattice is continuous and defect-free throughout its volume, providing unique mechanical, optical, and electrical properties. Examples include quartz, salt, diamond, and topaz.

Crystal growth techniques depend on material properties such as melting point, solubility, and volatility. Major methods include:

- **Growth from melt:** crystallization by cooling a melt (Bridgmann, Czochralski, Vernuil, zone melting, Kyropoulos, and skull melting).
- **Growth from vapour:** chemical or physical transport from a hot source to a cooler region, used for materials like ZnS and CdS.
- **Growth from solution:** low-temperature (slow cooling, solvent evaporation, temperature gradient) and high-temperature (flux growth) methods.
- **Solid-state single crystal growth (SSCG):** cost-effective for complex compositions, controlling grain growth and microstructure through the mixed control mechanism [11].

L-Asparagine Monohydrate (LAM) is an organic compound, formula $(NH_2)\ COCH_2CH\ (NH_2)\ COOH{\cdot}H_2O$, colourless and transparent, melting at 234–235°C, with molar mass 150.14 g/mol. It is structurally similar to L-Aspartic acid and is used in biomanufacturing and biochemical applications.

Potassium Iodide (KI) is a white, odourless solid, formula KI, melting point 681°C, molar mass 166.0028 g/mol, and soluble in water. It is used medically for hyperthyroidism, radiation protection, and certain skin conditions. Industrially, KI is produced by reacting potassium hydroxide with iodine:

$$\mathbf{2\ KOH + I_2 \rightarrow KI + H_2O + KIO}$$

Excessive or long-term exposure to KI may cause iodine poisoning, skin irritation, or allergic reactions.

REVIEW OF LITERATURE

L. Gobinathan and Boopathy (2015) explored the influence of potassium iodide (KI) on the growth behavior of L-asparagine monohydrate (LAM) crystals using the slow-evaporation method from aqueous solution [6]. Their study showed that both pure and KI-incorporated crystals exhibited good transparency and well-formed external morphology. EDAX analysis verified the inclusion of KI within the LAM host lattice. Microhardness measurements suggested that although the crystals maintained considerable mechanical strength, the addition of KI caused a slight reduction in hardness compared to the undoped sample. Etch pattern observations also indicated acceptable crystalline perfection in the doped crystals.

G. Kanagan et al. (2019) reported the growth and detailed evaluation of optical and thermal behaviors of L-asparagine monohydrate–potassium iodide (LAMPI) single crystals synthesized by slow evaporation [8]. Single-crystal XRD analysis confirmed an orthorhombic crystalline arrangement with a non-centrosymmetric space group, while powder XRD verified the crystalline phase purity. Their investigation further covered optical transmittance, thermal stability, and SHG efficiency, demonstrating the material's suitability for nonlinear optical (NLO) applications.

Elanthiraiyan et al. (2019) grew semi-organic LAMPI crystals via solvent evaporation and conducted comprehensive spectroscopic and physicochemical studies [4]. FTIR spectral analysis confirmed the expected functional groups and vibrational modes. Notably, the SHG efficiency of the LAMPI crystal was reported to be approximately 8.6 times higher than that of KDP. Additional characterization, including Vickers microhardness, TG–DTG thermal analysis, fluorescence spectroscopy, and dielectric studies, highlighted the potential of the material in optical and electronic device applications.

M. Dinesh Raja et al. (2020) further extended the work on LAM–KI crystals grown through slow evaporation and focused on their structural, optical, and thermal properties [9]. Their findings confirmed the presence of characteristic functional groups, and optical measurements indicated a favourable band-gap value suitable for optoelectronic and photonic devices. SHG testing confirmed the nonlinear optical activity of the synthesized material.

Together, these studies indicate that KI-modified L-asparagine monohydrate crystals exhibit enhanced optical transmittance, improved SHG response, and stable mechanical and thermal behaviour, making them strong candidates for future NLO and optoelectronic applications.

SYNTHESIS AND EXPERIMENTAL TECHNIQUE

SYNTHESIS

L-Asparagine monohydrate (LAM) and potassium iodide (KI) were selected as starting materials for the growth of both pure and KI-doped LAM single crystals. A saturated aqueous solution of L-asparagine monohydrate was initially prepared at ambient temperature. The mixture was stirred for several hours using a magnetic stirrer to ensure complete dissolution, after which it was filtered through Whatman filter paper to remove any undissolved impurities. The clear solution obtained was then left undisturbed in a dust-free environment to facilitate slow evaporation. Transparent and defect-free LAM single crystals were collected after approximately 4–5 days of growth. The reaction involved in the formation of the pure compound is represented as:

$$C_4H_{10}N_2O_4 + H_2O \rightarrow C_4H_{12}N_2O_5$$

The same growth procedure was adopted to obtain KI-doped LAM crystals with doping concentrations of 0.01 mol%, 0.03 mol%, and 0.05 mol%. The doped solutions were similarly allowed to undergo slow evaporation, resulting in good-quality crystals after 4–5 days. The reaction for the doped system may be expressed as:

$$C_4H_{10}N_2O_4 + KI \rightarrow C_4H_{10}N_2O_4 \cdot KI$$

CONSTANT TEMPERATURE WATER BATH

A constant-temperature water bath was employed to support the slow-evaporation, low-temperature crystal-growth process. This apparatus consists of a water-filled chamber equipped with a programmable heating system located at its base, enabling precise control of solution temperature during growth. A schematic representation of the water bath is shown below.

In general, a water bath is a widely used laboratory device designed to maintain samples at a stable and uniform temperature for extended periods. Depending on the model, users can adjust the required temperature through either a digital or analog control interface. Typical applications of a water bath include warming chemical reagents, melting substrates, incubating biological samples, and facilitating reactions that require elevated or constant temperatures. In the present study, the constant-temperature water bath ensured controlled evaporation of the prepared solutions, thereby promoting the growth of high-quality single crystals.

Fig. (1) Constant Temperature Water Bath

CHARACTERIZATION

X-RAY DIFFRACTION (XRD)

The grown crystals were subjected to various characterization techniques to analyze their structural, optical, and physicochemical properties. The methods employed in the present work are described below.

Because the wavelength of X-rays is comparable to interatomic distances, X-ray diffraction is an ideal technique for studying the structural arrangement of atoms in crystalline materials. Due to their high energy, X-rays can penetrate well into the sample and provide information about the bulk crystal structure. When an X-ray beam interacts with a crystal, the crystal behaves like a three-dimensional diffraction grating, producing diffracted beams at specific angles. These diffraction angles are recorded to obtain the XRD pattern.

The peak positions in the diffraction pattern provide information about the unit cell dimensions, phase identification, crystal system, space-group symmetry, and translational periodicity. In addition, the peak profile—particularly the full width at half maximum (FWHM)—can be used to estimate crystallite size and assess structural quality.

In this work, XRD measurements were carried out using a Rigaku Miniflex II X-ray diffractometer equipped with Cu Kα radiation. The optical photograph of the instrument is shown in Figure 2.

Fig. (2) X-Ray diffractometer (Rigaku Miniflex II, Japan)

UV–VISIBLE SPECTROSCOPY (UV–VIS)

UV–Visible spectroscopy is a widely used analytical method for studying the absorption characteristics of materials in the ultraviolet and visible regions of the electromagnetic spectrum. This technique is particularly valuable because many molecules absorb light in these regions due to electronic transitions involving π-electrons and non-bonding electrons. Absorption in the visible region directly influences the color of the compound, while absorption in the UV region provides insight into electronic structure.

The UV–Visible absorption data were recorded using the BLACK-Comet spectrometer system, which offers research-grade performance in a compact, robust design. The instrument provides standard spectral analysis tools such as peak wavelength, FWHM, and centroid determination, along with additional features including baseline correction, data smoothing, spectral derivatives, and episodic data capture.

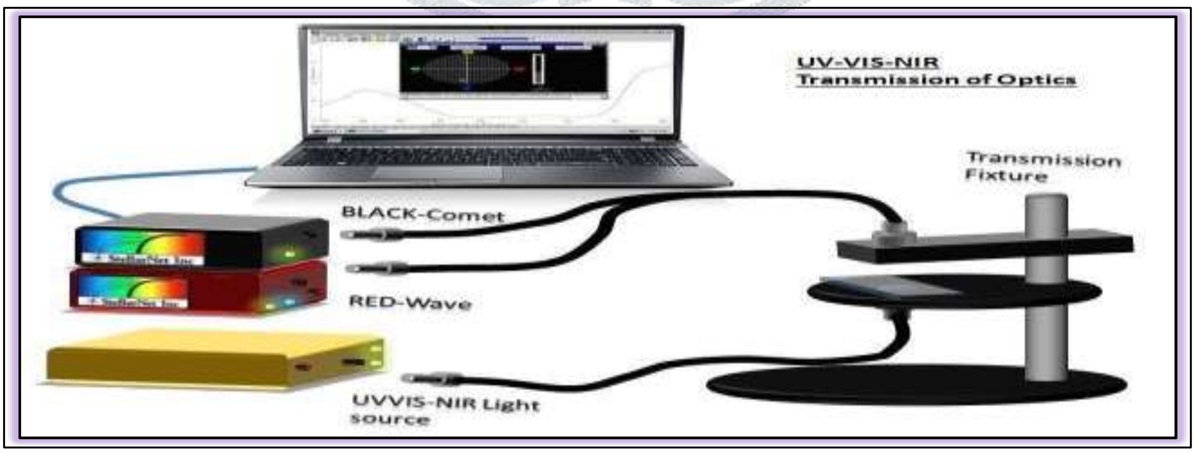

Fig. (3) UV-Visible Spectroscopy (Black-Comet-SR, StellarNet Inc., USA).

RESULTS AND DISCUSSION

Pure and KI-doped L-asparagine monohydrate (LAM) single crystals were successfully grown by the slow evaporation technique. The harvested crystals exhibited good transparency and well-defined morphology. The optical photographs of the grown pure and doped LAM crystals are shown in the figures below.

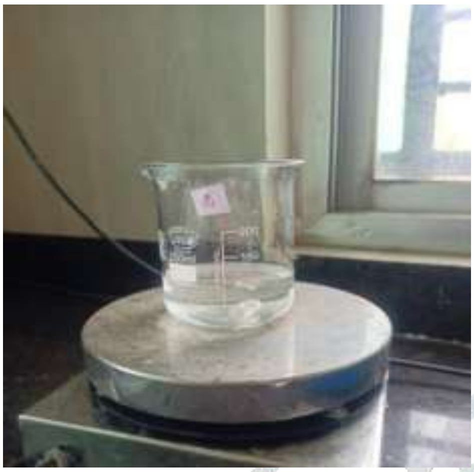

Fig. (4) LAM Crystal

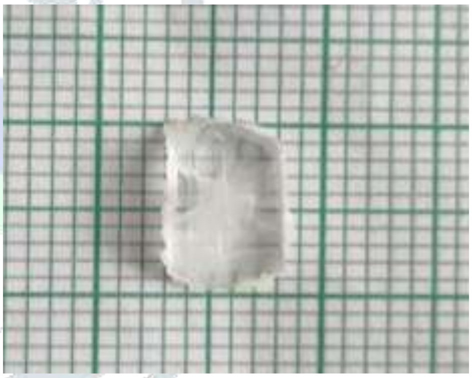

Fig. (5) 1% KI-doped LAM.

Fig. (6) 3% KI doped LAM

Fig. (7) 5% KI doped LAM

UV–VISIBLE SPECTROSCOPY

UV–Visible–NIR spectral analysis of the LAMPI crystals was carried out in the wavelength range of 200–1000 nm. The absorption and transmission characteristics of the pure and KI-doped samples were recorded, with detailed transmittance measurements taken between 200 and 750 nm. The pure LAM crystal exhibited a maximum transmittance of approximately 50%. In comparison, the 1%, 3%, and 5% KI-doped LAMPI crystals showed reduced transmittance values of around 40%, 30%, and 10%, respectively.

Among the doped samples, the 1% KI-doped crystal displayed the highest transmittance, indicating better optical clarity relative to the higher doping concentrations. Overall, the LAMPI crystals demonstrated good transparency in both the UV and visible regions, confirming their potential suitability for optical and optoelectronic applications. The transmittance spectra for the samples are presented in Figure 8, while the corresponding absorption spectra and calculated optical band gap values for pure and doped crystals are shown in Figure 9.

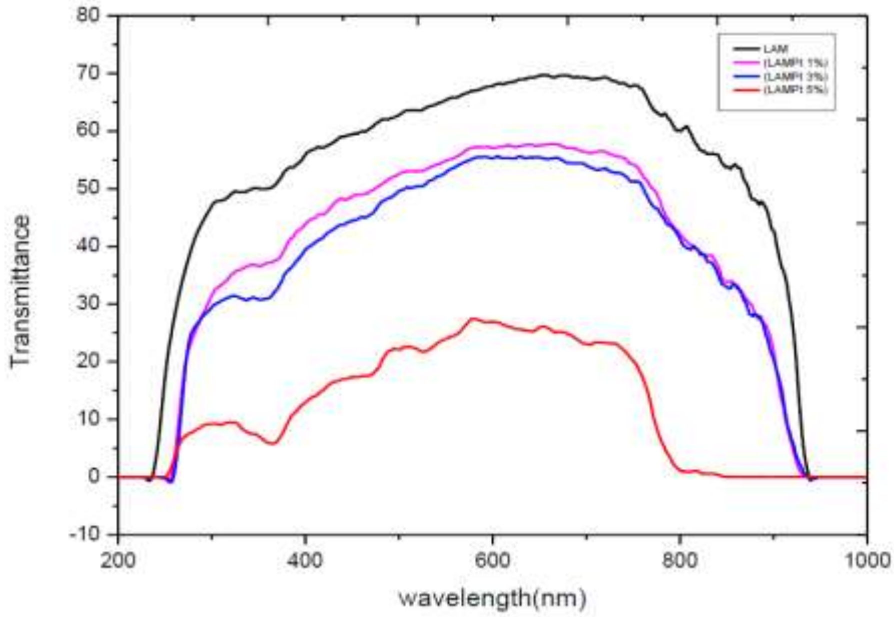

Fig.(8) Transmittance spectra of pure and doped LAM

BAND GAP

The optical band gap values of the pure and KI-doped LAM crystals were determined from their UV–Visible absorption spectra using the Tauc plot method. The pure LAM crystal exhibited a band gap of approximately 4.9 eV. For the doped samples, the band gap decreased slightly with increasing KI concentration, showing values of about 4.6 eV for the 1% KI-doped crystal and 4.5 eV for the 3% KI-doped crystal. This reduction in band gap with doping indicates a slight modification in the electronic structure of the material, which can be beneficial for enhancing its performance in optoelectronic applications.

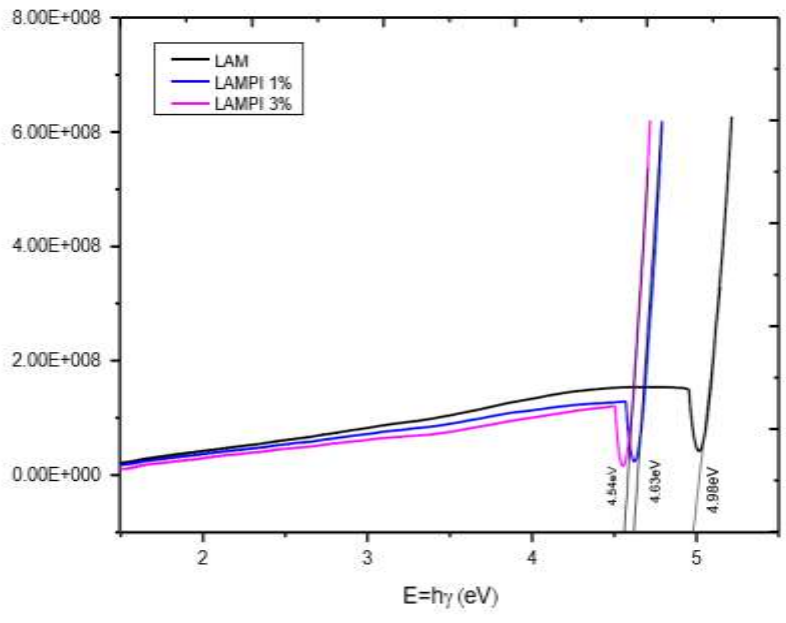

Fig. (9) Energy band gap of pure and doped LAM

XRD Study

The grown LAMPI crystals were analyzed using a powder X-ray diffractometer to determine their structural properties. The powder XRD pattern confirms that the crystals crystallize in an orthorhombic system with a non-centrosymmetric space group. The presence of sharp, well-defined diffraction peaks at specific 2θ values indicates good crystalline quality and an ordered lattice arrangement. Similar diffraction features were observed for the 1%, 3%, and 5% KI-doped LAMPI crystals, showing that doping does not significantly alter the fundamental crystal structure. The recorded XRD pattern for the samples is presented in Figure 10.

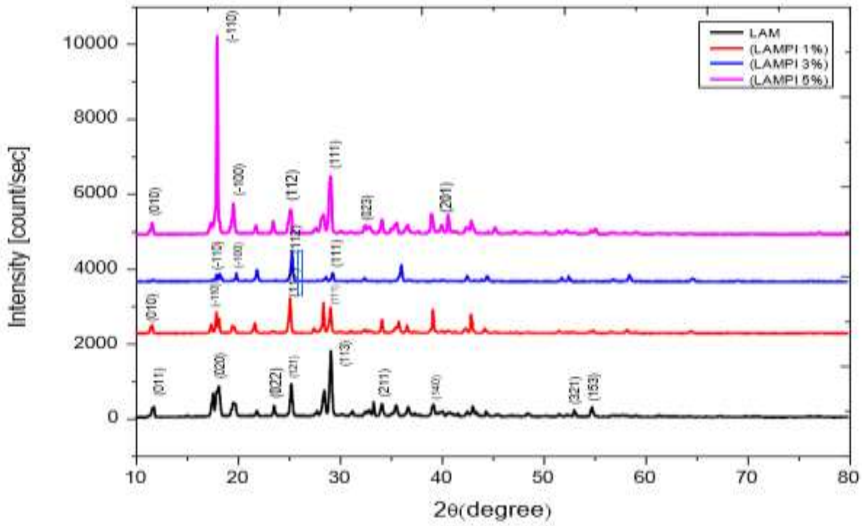

Fig.(10)X-Ray diffraction pattern of pure and doped LAM

CONCLUSION

Semi-organic L-asparagine monohydrate crystals blended with potassium iodide (LAMPI) were successfully grown using the slow evaporation technique. Based on the characterization results, it can be concluded that the grown crystals exhibit high optical quality, and the addition of KI dopant enhances both optical transparency and functional performance. Single-crystal XRD analysis confirmed that the crystals crystallize in an orthorhombic system with a non-centrosymmetric space group. Powder XRD further confirmed the material's crystalline nature. Optical studies indicated that the energy band gap of pure LAM is approximately 4.9 eV. In comparison, the 1% and 3% KI-doped crystals show band gaps of 4.6 eV and 4.5 eV, respectively, as determined using the Tauc plot method.

FUTURE SCOPE

Crystals such as LAMPI have a wide range of potential applications. In the future, this growth technique can be applied to develop advanced optical devices, including high-power lasers. These materials are also highly relevant in the field of nonlinear optics, with applications in optical data storage, optical information processing, and electro-optic switching. By incorporating dopants such as neodymium, it is possible to grow high-quality crystals with enhanced functional properties. Such materials have been successfully employed for second harmonic generation, frequency doubling of Nd: YAG lasers, and other electro-optical applications. Organic and semi-organic crystals are increasingly of interest due to their ability to efficiently double the frequency of laser light and facilitate high-speed optical data processing, which is critical for modern technologies such as optical computing and optical telecommunication systems.

REFERENCES

[1] P. N. Prasad, *Nanophotonics*. Hoboken, NJ, USA: Wiley, 2004.
[2] S. Manikandan, R. Mahalakshmi, P. Krishnan, F. Yogam, and P. Rajesh, "Growth, structural, optical, thermal, and dielectric properties of L-asparagine monohydrate admixture L-thiomalic acid single crystal," *Optik – International Journal for Light and Electron Optics*, 2016.

[3] F. Yogam, I. Vetha Potheher, R. Jeyasekaran, M. Vimalan, M. Antony Arockiaraj, and P. Saga, “Growth, thermal, and optical properties of L-asparagine monohydrate NLO single crystal,” *Journal of Thermal Analysis and Calorimetry*, Dec. 2013.

[4] M. Elanthiraiyan, M. Kandasamy, G. Kanagan, G. Govindarajan, S. Paris, and R. Sambasivam, “Growth and some characterization of L-asparagine monohydrate potassium iodide (LAMPI) crystals,” *Compliance Engineering Journal*, vol. 10, no. 9, pp. 0898–3577, 2019.

[5] G. R. Meredith, “Nonlinear optical properties of organic and polymer materials,” in *ACS Symposium Series*, D. J. Williams, Ed., 1982.

[6] L. Gobinathan and K. Boopathy, “Effect of potassium iodide on the growth and characterization of L-asparagine monohydrate single crystals,” *Der Pharma Chemica*, vol. 7, no. 11, pp. 362–367, 2015.

[7] P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*. New York, NY, USA: Wiley, 1991.

[8] G. Kanagan, M. Kandasamy, G. Govindarajan, S. Pari, and R. Sambasivam, “Growth and characterization, optical, thermal properties of L-asparagines monohydrate potassium iodide (LAMPI) NLO crystals,” *Journal of Information and Computer Science*, vol. 9, no. 9, pp. 1548–7741, 2019.

[9] M. Dinesh Raja, S. Pari, G. Kanaga, G. Satheesh Kumar, and P. Christuraj, “Investigation on structural, optical, and thermal properties of L-asparagine monohydrate potassium iodide (LAMPI) NLO crystals,” *Materials Today: Proceedings*, 2020.

[10] Y. Zhang, Y. Wang, Y. Che, and J. Zheng, “Crystal growth studies,” *Journal of Crystal Growth*, pp. 120–124, 2007.

[11] M. Shakir, B. Riscob, K. K. Maurya, V. Ganesh, M. A. Wahab, and G. Bhagavannarayana, “Unidirectional growth of L-asparagine monohydrate single crystal: First-time observation of NLO nature and studies on crystalline perfection, optical, mechanical and dielectric properties,” *Journal of Crystal Growth*, vol. 312, pp. 3171–3177, 2013.

[12] I. Milisavljevic and Y. Wu, “Current status of solid-state single crystal growth,” *BMC Materials*.

[13] “Second harmonic generation,” *Wikipedia, The Free Encyclopedia*. Accessed: [Online]. Available: https://en.wikipedia.org/wiki/Second-harmonic_generation.

[14]V. R. Sagane, G. Vinitha, G. G. Muley and P. M. Wankhade, “Influence of pH on growth, structural, thermal, linear and nonlinear optical properties of L-asparagine monohydrate single crystal,” *Phys. Open*, vol. 20, p. 100224, 2024.