



## Synthesis, growth and characterization studies on L-arginine and dinitrate

B Ashwini<sup>1</sup>, Dr. D Mohan Radheep<sup>2</sup>

<sup>1</sup> M. Phil, Research Scholar, Department of Physics, Prist University Puducherry, Tamil Nadu, India

<sup>2</sup> Ph.D., Associate Professor and Head, Department of Physics, PRIST University, Puducherry, Tamil Nadu, India

### Abstract

We live in a nonlinear world. While linearization beautifies physics, nonlinearity provides excitement in physics. In recent years, significant advances have been made in the field of nonlinear optics and optical computing. These areas have grown rapidly in the last decade, so that today these have emerged as important disciplines in their own right. Optics is already preferred for many applications owing to its wide bandwidth and autonomy from electromagnetic interference. Since fiber optic cable has low absorption, they can transmit signals for several kilometers, but the signal must be amplified. It is more efficient if the light beam is amplified directly by a laser beam in a suitable medium. Such a process has come into the realm of nonlinear optics. The science that deals with the interactions of a laser beam with an optical medium is called nonlinear optics and the medium itself is called a non-linear optical (NLO) material.

Since the invention of the first laser 40 years ago, the frequency conversion of laser radiation in nonlinear optical crystals has become an important technique widely used in quantum electronics and laser physics for solving various scientific and engineering problems. The fundamental physics of the wave light interactions in nonlinear optical crystals is now largely understood.

**Keywords:** electromagnetic waves, optical crystals, nonlinear optics, optical computing, ultraviolet

### 1. Introduction

This has enabled the production of the various harmonic generators, sum and difference frequency generators, and parametric oscillators based on nonlinear crystals that are now commercially available. At the same time, scientists continue an active search for novel high-frequency optical materials. The propagation of electromagnetic waves through nonlinear media gives rise to vibrations at harmonics of the fundamental frequency, at sum and difference frequencies, and so on. When one or more sufficiently powerful beams of laser radiation pass through the dielectrics, the frequency of the radiation may be transformed to the second, third and higher harmonics and to combination (sum and difference) frequencies. In this way, the range of wavelengths generated by a certain laser source can be considerably increased.

Now, after 40 years of research with NLO materials, it is possible to cover almost continuously the range from 170 nm to 18  $\mu\text{m}$ . Furthermore, the transparency region of NLO crystals now reaches 165 nm to 125  $\mu\text{m}$ . As a result, further extension of applications to the ultraviolet (UV) and far-infrared regions will be possible. However, materials limitations are significantly slowing the development of required optical devices.

The 'ideal' nonlinear crystal does not exist. Only a very few crystals in practice are found to satisfy the major requirements and out of thousands of nonlinear crystals studied, only a handful of crystals have been found to be suitable in some way or other. The applicability of a particular crystal depends on the nonlinear process used, the desired device characteristics and the pump laser. Special material properties that are important in one application may not be significant in

another. For a material that has favourable features such as large nonlinearity, high damage threshold, favourable crystal growth habits etc., an application can invariably be found that uses the crystal efficiently.

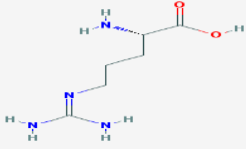
During the last four decades, optics has made rapid inroads into application areas previously dominated by electronics. In applications where bandwidth and electrical interference are presenting severe limitations on electronics, fiber based communication systems are considered as viable alternatives. The study of linear and nonlinear optical properties of materials has led to the development of a large number of optical devices. Nonlinear optical materials will be the key elements for future photonic technologies because of the fact that photons are capable of carrying information at the speed of light. It may be stated without doubt that while electronics revolution dominated the twentieth century technologies, it is strongly believed that photonics may dictate the technological trends in the twenty first century. A nonlinear optical material has many applications. Materials which can generate highly efficient second harmonic light by laser are of great interest in various applications including telecommunications, optical computing, optical information processing, optical disk, laser remote sensing, laser driven fusion, color displays and medical diagnostics. Materials with large nonlinearities, short transparency cut-off wavelengths and with stable physicochemical properties are needed for these applications. Single crystals play a vital role in most of the optics based applications. So the growth of single crystals and their characterization towards device fabrication are important in both basic and applied research. Crystal growth is an interdisciplinary subject covering physics, chemistry,

electrical engineering, metallurgy, crystallography, mineralogy etc. In the past few decades, there has been a growing interest in crystal growth process, particularly in view of the increasing demand for materials for technological applications. The strong influence of single crystals in the present day technology is evident from the 5 recent advancements in the fields of semiconductors, polarizers, transducers, infrared detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, nonlinear optic, piezoelectric, acousto-optic, photosensitive materials and crystalline thin films and the computer industry. Hence, to achieve higher performance in the fabricated devices, good quality single crystals are needed.

In this chapter, the author discusses the development of the nonlinear optical crystals along with the theory of nonlinear optics and the various methods of growing these crystals and in particular the solution growth method.

## 2. Materials and Methods

**Table 1:** L-Arginine Properties

Chemical Name	L-arginine
Molecular Formula	C <sub>6</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub>
Molecular Weight	174.204 g/mol
Structure	
Physical Description	Solid
Melting Point	244 Degree Celsius
Solubility	Water Solubility 182000 mg/L (at 25 °C) slightly soluble in ethanol
Exact Mass	174.112 g/mol
Complexity	176
Compound Is Canonicalized	True

L-Arginine is an essential amino acid that is physiologically active in the L-form.

L-Arginine is an essential amino acid in juvenile humans, L-Arginine is a complex amino acid, often found at active site in proteins and enzymes due to its amine-containing side chain. L-Arginine may prevent or treat heart and circulatory diseases, combat fatigue, and stimulate the immune system. It also boosts production of nitric oxide, relaxing blood vessels, and treating angina and other cardiovascular problems. L-Arginine is also an important intermediate in the urea cycle and in detoxification of nitrogenous wastes. (NCI04)

L-Arginine is an essential amino acid that is physiologically active in the L-form. In mammals, L-arginine is formally classified as a semi essential or conditionally essential amino acid, depending on the developmental stage and health status of the individual. Infants are unable to effectively synthesize L-arginine, making it nutritionally essential for infants. Adults, however, are able to synthesize L-arginine in the urea cycle.


Arginine can be considered to be a basic amino acid as the

part of the side chain nearest to the backbone is long, carbon-containing and hydrophobic, whereas the end of the side chain is a complex guanidinium group. With a pKa of 12.48, the guanidinium group is positively charged in neutral, acidic and even most basic environments. Because of the conjugation between the double bond and the nitrogen lone pairs, the positive charge is delocalized. This group is able to form multiple H-bonds.

L-arginine is an amino acid that has numerous functions in the body. It helps dispose of ammonia, is used to make compounds such as nitric oxide, creatine, L-glutamate, L-proline, and it can be converted to glucose and glycogen if needed. In large doses, L-arginine also stimulates the release of hormones growth hormone and prolactin. L-Arginine is a known inducer of mTOR (mammalian target of rapamycin) and is responsible for inducing protein synthesis through the mTOR pathway. mTOR inhibition by rapamycin partially reduces L-arginine-induced protein synthesis. Catabolic disease states such as sepsis, injury, and cancer cause an increase in L-arginine utilization, which can exceed normal body production, leading to L-arginine depletion.

Arginine also activates AMP kinase (AMPK) which then stimulates skeletal muscle fatty acid oxidation and muscle glucose uptake, thereby increasing insulin secretion by pancreatic beta-cell Arginine is found in plant and animal proteins, such as dairy products, meat, poultry, fish, and nuts. The ratio of L-arginine to lysine is also important - soy and other plant proteins have more L-arginine than animal sources of protein.

**Table 2:** Dinitrate Properties

Chemical Name	Dinitrate
Molecular Formula	-2 N <sub>2</sub> O <sub>6</sub>
Molecular Weight	124.008 g/mol
Structure	
Exact Mass	123.976 g/mol
Complexity	18.8
Compound Is Canonicalized	True

### 2.1 Methods of crystal growth

The consistency in the characteristics of devices fabricated from the crystals depends on the homogeneity and defect contents of the crystals. Hence, the process of producing single crystals, which offers a homogeneous media in the atomic level with directional properties, attracts more attention than any other process. The methods of growing crystals are very wide and mainly dictated by the characteristics of the material and its size<sup>[1]</sup>. The methods of growing single crystals may be classified according to their phase transformation as given below.

Growth from Solid Solid → solid phase transformation

Growth from liquid Liquid → solid phase transformation

Growth from vapour Vapour → solid phase transformation

The conversion of a polycrystalline piece of material into a single crystal by causing the grain boundaries to be swept through and pushed out of the crystal takes place in the solid-growth of crystals.

An efficient process is one, which produces crystals adequate for their use at a minimum cost. The growth method is essential because it suggests the possible impurity and other defect concentrations. Choosing the best method to grow a given material depends on material characteristics.

### 2.1.1 Growth from solution

The crystal growth from liquid can be classified into four categories namely

- a. Melt growth
- b. High temperature solution growth (Flux growth)
- c. Hydrothermal growth and
- d. Low temperature solution growth

There are a number of growth methods in each category. Among the various methods of growing single crystals, solution growth at low temperature occupies a prominent place owing to its versatility and simplicity. Growth from solution occurs close to equilibrium conditions and hence crystals of liquid perfection can be grown. Study of anisotropy of the properties of crystals requires specimens cut in different orientations from the same single crystal. This can be easily done from crystals of large size.

### 2.1.2 Growth from melt

This method is very popular because the growth rate of crystals grown by this method is quite high. The preferential role of the electrochemical process responsible for the change in composition of the crystals when they grow in melt in an applied field has been studied [2]. In this method, the following popular techniques are used.

- a. Bridgman technique
- b. Czochralski technique
- c. Zone melting technique and
- d. Verneuil technique

### 2.1.3 High temperature growth (Flux Growth)

Flux and hydrothermal growths form the category of high temperature solution growth. In this method, a solid (molten salt/flux) is used as the solvent and the growth takes place well below the melting point [3] of the solute. This technique can be applied to incongruent melting materials. Mixed crystals of solid solution can also be grown by the choice of optimum growth parameters.

This technique can be used for the crystallization of oxide compounds which generally have high melting points as well as for materials which have phase transitions below the melting point [4]. The crystals grown from melt will have lower concentration of equilibrium defects and lower dislocation density

### 2.1.4 Hydrothermal growth

A number of metals, metal oxides and other compounds, practically insoluble in water up to its boiling point, show an appreciable solubility when the temperature and pressure are increased well above 100 °C and 1 atmosphere respectively.

The requirements of high pressure cause practical difficulties and there are only a few crystals of good quality and large size grown by this technique. Quartz is the crystal grown industrially by this technique.

### 2.1.5 Low temperature solution growth

Low temperature solution growth is the most widely used method for the growth of single crystals, when the starting materials are unstable at high temperatures [5]. This method demands that the materials must crystallize from solution with prismatic morphology. In general, this method involves seeded growth from a saturated solution. The driving force i.e., the supersaturation is achieved either by temperature lowering or by solvent evaporation. This method is widely used to grow bulk crystals, which have high solubility and have variation in solubility with temperature [6]. After many modifications and refinements, the process of solution growth now yields good quality crystals for a variety of applications. Growth of crystals from solution at room temperature has many advantages over other growth methods though the rate of crystallization is slow. Since growth is carried out at room temperature, the structural imperfections in solution grown crystals are relatively low.

Low temperature solution growth can be subdivided into the following methods:

- a. Slow cooling technique
- b. Slow evaporation technique and
- c. Temperature gradient technique

### 2.1.6 Slow cooling method

This is the most suitable method among various methods of solution growth. However, the main disadvantage of slow cooling method is the need to use a range of temperatures. The possible range of temperature is usually narrow and hence much of the solute remains in the solution at the end of the growth run. To compensate this effect, large volume of solution is required. The use of wide range of temperature may not be desirable because the properties of the grown crystals may vary with temperature. Temperature stability may be increased by keeping the solution in large water bath or by using a vacuum jacket. Achieving the desired rate of cooling is a major technological difficulty. This technique needs only a vessel for the solution in which the crystals grow. The height, radius and volume of the vessel are so chosen as to achieve the required thermal stability. Even though this method has technical difficulty of requiring a programmable temperature controller, it is widely used with great success.

### 2.1.7 Slow evaporation technique

As far as apparatus is concerned, slow cooling and slow evaporation methods are similar in nature. In this method, the saturated solution is kept at a particular temperature and provision is made for evaporation. If the solvent is non-toxic like water, it is desirable to allow evaporation into the open atmosphere. Typical growth conditions involve a temperature stabilization of about 0.05°C and rate of evaporation of a few mm<sup>3</sup>/h. The evaporation technique has an advantage viz. the crystals grow at a fixed temperature. But inadequacies of the temperature control system still have a major effect on the growth rate. This method can effectively be used for materials

having very low temperature coefficient of solubility. But the crystals tend to be less pure than the crystals produced by slow cooling technique, as the size of the crystal increases more impurities find place in the crystal faces. Evaporation of solvent from the surface of the solution produces high local super saturation and unwanted nuclei are formed. Small crystals are also formed on the walls of the vessel near the surface of the liquid from the material left after evaporation. They tend to fall into the solution and hinder the growth of the crystal. Another disadvantage lies in controlling the rate of evaporation. A variable rate of evaporation may affect the quality of the crystal. In spite of all these disadvantages, this is simple and convenient technique of growing single crystals of large size.

### 2.1.8 Temperature gradient method

This method involves the transport of the materials from hot region containing the source material to be grown to a cooler region where the solution is supersaturated and the crystal grows.

### 2.1.9 Gel growth

This is a very convenient laboratory process. Henisch (1988) [7] gave an excellent survey of the process. Only small crystals can be grown by this technique. Gels are two-phase systems comprising a porous solid with liquid filled pores. The pore dimensions depend on the concentration of the gel material. The most frequently used gels are based on silica. But gels based on gelatine, various soft soaps and pectin are also used. Seed crystals should be used to reduce flaws in the center of the crystals. It is very important to provide constant ambient temperature. It has been shown that the application of electric fields within the gel can influence the crystal growth processes.

## 3. Conclusion

Single crystals of L-argininium dinitrate (LADN) were grown by slow evaporation technique within a period of 30-35 days. The single crystal XRD data proves that LADN crystal is monoclinic in structure with space group of P21. The FT-IR studies confirm the existence of L-arginine in its salt form with nitric acid. From the optical absorption study confirm that the crystal has lower cut off wavelength 230 nm and which reveals that the crystal is highly suitable for NLO application. Dielectric studies infer the possible usage of LADN for photonics devices. The negative photoconductivity nature of LADN is revealed by photoconductivity investigations. The mechanical behavior of the LADN crystal shows that the LADN belongs to the hard category.

## 4. References

1. Ramasamy S, Sridhar B, Rama Krishnan V, Rajaram RK. 'L- Argininium dinitrate', Acta Cryst. E57. 2001; 0872-0874.
2. Kurtz SK, Perry TT. A Powder technique for the evaluation of nonlinear optical materials' J Appl. Phys. 1968; 39:3798-3813.
3. Rao KV, Smakula A. Dielectric properties of Cobalt oxide, Nickel Oxide and their mixed crystals', J Applied Physics. 1965; 36:2031-2038.

4. Bube RH. Photoconductivity of Solids, Wiley Interscience, New York, 1981.
5. Joshi VN. Photoconductivity', Marcel Dekker, New York, 1990.