

**SHORT AND ULTRA-SHORT LASER-INDUCED
SHOCK WAVE CRYSTALLIZATION OF
NITRATES**

BY

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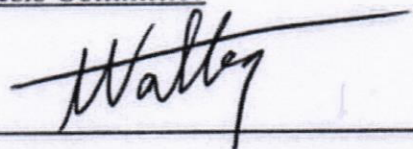
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*I dedicate this work to my parents and brother; may Allah accept and
forgive them and bring us together with them in the highest gardens of
paradise*

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Acronyms

CW : Continuous Wave

NaNO_3 : Sodium Nitrate

KNO_3 : Potassium Nitrate

$\text{Ca}(\text{NO}_3)_2$: Calcium Nitrate

Nd:YAG : Neodymium-doped Yttrium Aluminum Garnet

PBM : Population Balance Model

KCL : Potassium Chloride

NPLIN : Non-photochemical Laser Induced Nucleation

CNT : Classical Nucleation Theory

MOC : Method of Characteristics

ODE : Ordinary Differential Equation

DPO : Digital Phosphor Oscilloscope

XRD : X-Ray Diffraction

PLM : Polarized Light Microscope

SEM : Scanning Electron Microscope

THESIS ABSTRACT

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Laser-induced shockwave crystallization is an innovative method that uses short laser pulses to trigger clustering and sustain crystal growth. In this work, we designed and built a laser-induced crystallization system that utilizes both femtosecond and nanosecond laser pulses at 400 nm and 532 nm, respectively, to induce crystallization in nitrate solutions. Two experimental approaches were explored: direct laser induction via photochemical interaction and indirect induction using photochemically free shockwaves. The resulting crystals were analyzed for their size, size distribution, and shape using X-ray diffraction (XRD) and a polarized light microscope (PLM). The correlation between the shape and size of the crystals and factors such as laser energy, exposure time, and solution saturation levels was thoroughly investigated. Additionally, we conducted real-time monitoring of the clustering process by observing the

speed of sound in dissolved nitrate salts at different saturation levels, providing a dynamic view of the crystallization process.

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التبلور الناجم عن الصدمة الليزرية هو طريقة مبتكرة تستخدم نبضات ليزرية قصيرة لتحفيز التكتل ودعم نمو البلورة. في هذا العمل، قمنا بتصميم وبناء نظام تبلور مُستحث بالليزر يستخدم نبضات ليزر الفموتو ثانية والنانوثانية عند 400 نانومتر و 532 نانومتر على التوالي، لتحريض التبلور في محاليل اللترات. تم استخدام نهجين تجريبيين: الحث المباشر بالليزر عن طريق التفاعل الضوئي الكيميائي، والحث غير المباشر باستخدام موجات الصدمة الحرة الضوئية الكيميائية. تم تحليل البلورات الناتجة من حيث حجمها وتوزيع حجمها وشكلها باستخدام حيود الأشعة السينية (XRD) ومجهر الضوء المستقطب (PLM). تم التحقيق بدقة في العلاقة بين شكل وحجم البلورات وعوامل مثل طاقة الليزر ووقت التعرض ومستويات تشبع المحلول. بالإضافة إلى ذلك، أجرينا مراقبة في الوقت الفعلي لعملية التكتل من خلال مراقبة سرعة الصوت في أملاح اللترات المذابة عند مستويات تشبع مختلفة، مما يوفر رؤية ديناميكية لعملية التبلور.

CHAPTER 1

INTRODUCTION

Crystallization plays a crucial role in many applications and significant amounts of crystalline materials are used by the pharmaceutical, chemical, and food sectors. In these sectors, crystallization is a crucial separation process that has a big impact on plant productivity and profitability. Two important key features of produced crystals is their size and distribution. Typically, the formation of crystals with a specific size distribution presents a significant difficulty for the commercial crystallization process [2].

The effectiveness and reproducibility of crystallization are often limited by crystal nucleation, a stochastic process that is typically unclear and frequently displays significant variability even under constant and well-controlled circumstances [3], [4]. There are several unconventional methods of producing crystals by involving external interventions such as sonication [5], nuclear radiation [6], and electromagnetic field [7]. These methods are in addition to the conventional crystallization, which occurs spontaneously when solutions are in a supersaturated state in which the solute concentration exceeds the solubility limit [8]. For instance, a research team has grown

sizable mercury thiolate crystals from liquid mercury using sonication within a very brief period of time [5]. Another study conducted by Shannon Mahurin et al irradiated solutions of sodium chlorate in water to alter the distribution of sodium chlorate isomeric crystals by first employing positrons from the nuclear decay of sodium-22 isotope and then very energetic beta particles from the nuclear decay of strontium-90 isotope [6].

When a solution is irradiated with strong laser pulses or with focused continuous-wave (CW) beams to induce nucleation, the process is known as laser-induced crystallization [1]. This photo-physical phenomenon was first described by Garetz and colleagues, where 1064 nm laser pulses was used to induce crystallization in an aqueous supersaturated urea solution. Later, Garetz and colleagues discovered that intense, brief 532 nm laser pulses were more successful for inducing non-photochemical laser-induced nucleation in lysozyme solutions [9]. In the same context, Nakamura et al. employed a supersaturated anthracene solution to examine the mechanism of femtosecond laser-induced crystallization. They reported that when a single-shot, high-energy femtosecond laser pulse (above $3.1 \mu\text{J}/\text{pulse}$) was directed into a sufficiently supersaturated solution, anthracene crystals were generated right away in the area of the laser focal point [10].

Also, various techniques have been used to induce nucleation using external disturbances, such as ultrasonic, mechanical shock, and electric fields [3], [11], [12]. One relatively unknown method for localizing the location of nucleation both temporally and spatially is laser-induced nucleation [13], [14]. Such control creates opportunities, such as studying the dynamics of nucleation or managing product uniformity during

the solids manufacturing process [15].

In this work, and in order to produce crystallization in saturated aqueous solutions of potassium nitrate (KNO_3), two types of lasers will be used: high intensity nanosecond Nd:YAG pulsed laser and ultrashort femtosecond laser. These crystals of nitrate salt have numerous uses in a variety of sectors, including food, agriculture, colors, and solar cells [16].

1.1 Objectives

The main objective of this work is to study the crystallization process of potassium nitrate (KNO_3), by using two types of lasers: nanosecond Nd:YAG pulsed laser and Sapphire femtosecond laser.

We have then identified specific objectives, which are to:

1. Design, build, and optimize experimental setup to induce crystallization in nitrates using photochemical and photochemical-free layouts.
2. Characterize grown nitrate crystals in term of shape, size, and shape distribution.
3. Investigate the effect of time elapsed after exposure to laser and laser energy on the shape, size, and size distribution of grown crystals.
4. Investigate the effectiveness of direct laser and shock-wave laser on the crystallization process in terms of crystal size and size distribution.

CHAPTER 2

LITERATURE REVIEW

Both nature and industry are rife with crystallization. In industrial practice, a wide range of essential items, including agrochemicals, medicines, and battery materials, are manufactured in crystalline form [17]. However, we still have a long way to go in terms of mastering the crystallization process on all stages, from the molecular to the macro levels. This bottleneck impedes not just our ability to engineer the qualities of crystalline products necessary for preserving our quality of life, but also the development of a resource recovery circular economy that is sustainable. Approaches utilizing light fields have come to light as intriguing alternatives to control crystallization in recent years [17].

Nowadays, lasers are frequently used in study fields like crystallization because of their extraordinary features. In lasers, the electromagnetic radiation is stimulated to emit light using an optical amplification process. As a result, a laser beam has distinct qualities that set it apart from other types of light, including monochromaticity, coherence, extremely high intensity, and low divergence.

Garetz et al. reported a novel approach using a laser to analyze second harmonic

production in supersaturated urea solution in water. They discovered the crystallization of urea crystals when they focused 1.06 μm Q-switched Nd:YAG laser pulses into a supersaturated solution of urea in water [18]. It was later concluded that the optical field of the laser light causes molecules in urea clusters to align optically with polarization, which causes the nucleation [10]. While 355-nm nanosecond pulsed laser irradiation was used to create dianthracene and benzopinacol crystals from anthracene and benzophenone solutions, Okutsu et al. demonstrated that photochemical mechanisms are responsible for light-induced crystallization and its morphological regulation [19], [20]. They also suggested a way for crystallizing proteins using intermediate radicals created by ultraviolet light as the crystallization's nucleus [21].

The femtosecond laser opens up more alternatives in addition to these crystallization method, using femtosecond laser irradiation, Yoshimura and colleagues have investigated the ideal laser settings to produce crystallization. They discovered via their investigation that the repetition rate affects the nucleation efficiency and that using a femtosecond laser results in high efficiency. Additionally, they extended their research to urea crystals and concluded that the crystallization was caused by a photomechanical reaction to femtosecond laser irradiation [22], [23]. Similar studies on femtosecond laser-induced crystallization in an anthracene supersaturated solution were carried out by Kazuhiko Nakamura et al. When a single femtosecond laser pulse with energy exceeding 3.1 $\mu\text{J}/\text{pulse}$ was directed into a highly supersaturated solution, anthracene crystallization occurred immediately near the laser's focal point. The crystallization threshold energy (3.1 $\mu\text{J}/\text{pulse}$) matched the energy required for laser-induced bubble formation, which involved sequential processes of shockwave emission,

cavitation bubble formation, and collapse. Additionally, higher pulse energy reduced the level of supersaturation needed for crystallization. These findings indicate that the crystallization process is initiated during bubble formation events. Additionally, it was discovered that crystallization was enhanced at the bubble’s surface [10]. In the same path, a femtosecond laser pulse was used by Hiroshi Y. Yoshikawa and his associates to regulate the development of crystals of urea in a highly saturated urea solution [23]. A new needle-like crystal began to develop from the laser’s focal point, which was around the size of a micrometer, when scientists focused a single 800 nm or 1470 nm femtosecond laser pulse at needle-like urea crystal through an objective lens. As the laser energy was increased, more of these crystals that were caused by the laser formed. However, such crystal formation was not induced by CW laser irradiation at 1480 nm. The same group were able to successfully shape the crystals using this novel phenomena. Finally, the mechanism of femtosecond laser-induced crystallization was examined, emphasizing crystal fragmentation driven by photomechanical effects [23].

Recently, using high-speed microscopy observations and 1D finite element simulations, Nagalingam and colleagues show that crystallization in supersaturated aqueous solutions of potassium chloride (KCl) can be caused by a brief rise in supersaturation around a laser-induced cavitation bubble. They discovered that crystallization from supersaturated aqueous solutions is induced by a cavitation bubble caused by a Nd:YAG laser pulse below breakdown threshold with supersaturation and laser-energy dependent nucleation kinetics. The quantity of crystals and their form are correlated with the features of the simulated supersaturation peak [24].

2.1 Nitrate Salts Properties

The possible use in energy systems has increased interest in the chemistry of sodium and potassium nitrate in recent years. Melted mixes of potassium and sodium nitrate, for instance, have been suggested for use in big solar power plants as high-temperature heat transfer fluid and storage media [25], [26]. These salts and their mixes are inexpensive, chemically stable, and largely non-corrosive—all qualities that are desirable for industrial fluids—and have low melting points (<520 K), also known as low temperature eutectics [27]. In addition, because potassium nitrate crystals grow like needles, we can easily study their growth.

2.2 Nucleation Theories

2.2.1 Classical Nucleation Theory (CNT)

A nucleus is viewed as a sphere of a condensed phase in the classical theory of nucleation, and its free energy is defined in terms of thermodynamics [3], [28]. The free energy $\Delta G(r)$ of a nucleus with radius r can be expressed as

$$\Delta G(r) = 4 \pi r^2 \gamma + \frac{4}{3} \pi r^3 \Delta G_v \quad (2.1)$$

where ΔG_v is the free energy per unit volume of a crystal, k is the Boltzmann constant, and γ the surface free energy per unit area. The supersaturation ratio of the solution S . Supersaturation occurs with a solution when the concentration of a solute exceeds

the concentration specified by the value of solubility curve, the temperature T , and its molecular volume v , all of which affect the free energy ΔG_v .

$$\Delta G_v = -\frac{k T \ln S}{v} \quad (2.2)$$

However, the extra free energy required for the nuclei's formation is imposed by the surface term. Nuclei smaller than a threshold radius r_c can only dissolve back into the solution as the monomers because this is the only way to reduce their free energy. The smallest size at which nuclei can remain stable and continue to expand (grow) is known as the critical radius.

The value of r_c can be found from the relation $d\Delta G/dr = 0$ at $r = r_c$, which gives a critical free energy ΔG_{crit} as:

$$r_c = -\frac{2 \gamma}{\Delta G_v} \quad (2.3)$$

$$\Delta G_{crit} = \frac{4}{3} \pi \gamma r_c^2 \quad (2.4)$$

By substituting the value of ΔG_v in equation 2.2 in equation 2.3 we get:

$$r_c = \frac{2 \gamma v}{k T \ln S} \quad (2.5)$$

The rate of nucleation of N particles as a function of time t can be found by the Arrhenius equation, in which A is a pre-exponential factor.

$$\frac{dN}{dt} = A \exp \left[-\frac{\Delta G_{crit}}{K_B T} \right] \quad (2.6)$$

By using equation 2.4 and equation 2.5 we get:

$$J = \frac{dN}{dt} = A \exp \left[\frac{16 \pi \gamma^3 v^2}{3 k^3 T^3 (\ln S)^2} \right] \quad (2.7)$$

Supersaturation and temperature are the two experimental parameters that can be changed from equation 2.7. The nucleation rate increases as these variables rise, although supersaturation has the biggest impact on the nucleation rate [29].

2.2.2 Population Balance Model (PBM)

A crystallization process typically involves a number of intricate processes, including nucleation, crystal development, aggregation, attrition, and crystal breakdown, etc [3], [30]. The simultaneous or successive nature of these occurrences makes it difficult to solve a full PBM [30]. The condensed 1D-PBM can be described as follows by taking into account the two main phenomena, nucleation and crystal growth, and neglecting the other terms:

$$\frac{\partial \psi(t, L)}{\partial t} + G(t, L) \frac{\partial \psi(t, L)}{\partial L} = 0 \quad (2.8)$$

Where $\psi(t, L)$ is represents the population density function, L represents the crystal length, and G represents the growth term and can be extracted from equation 2.9, the parameter K_g refers to the growth coefficient, and g is the order of the growth process, while w and w_{sat} are solute and saturated concentrations, respectively [30].

$$G(t) = K_g \left(\frac{w}{w_{sat}} - 1 \right)^g \quad (2.9)$$

All of the aforementioned processes should be included in a thorough explanation of the PBE for crystallization. Certain system assumptions have been made in order to simplify the PBE. For example, only taking into account nucleation and crystal development while ignoring other events, Czapla et al. [31] effectively described ammonium threonine crystallization techniques.

For a variety of reasons, it is challenging to numerically solve the population balance equation (PBE). Numerical instability and diffusion problems typically arise in the numerical solutions of PBEs for seeded batch systems. Incompatibility between the starting and boundary conditions is one potential cause of the already mentioned issue. It is unlikely that seeds will have a number density distribution that is identical to the nucleation process's output. The distribution's first-order derivative might not be the same if their values match. There may be abrupt discontinuities as a result, which numerical diffusion can swiftly widen. Another problem that occurs often when solving PBEs is the appearance of steep moving fronts, often known as a cause of numerical instability. This effect results from the growth-dominated process's convective character [32]. To address these complications, a number of researchers in this field have attempted to create specific algorithms. Numerous effective numerical approaches were introduced, including the finite difference methods [33], [34], the Monte Carlo method [35], the method of moments [36], and the method of characteristics (MOC), in which the provided PBE is converted into a set of ODEs, and then solved along the particle's travel lines (characteristic curves). The population is tracked with a speed that matches the growth rate after the particles are initially detected and recognized [2], [30].

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Sample Preparation

The potassium nitrate (KNO_3) samples of aqueous nitrate salt solutions were prepared individually by dissolving the salts in distilled hot water to ensure complete dissolvability. To distinguish between undersaturated, saturated, and supersaturated conditions, each sample was prepared at a different saturation level (concentration). The maximum amount of salts totally dissolved in a given amount of solvent is known as the saturation level. The more heat applied to aqueous nitrate salt solution, the more soluble it gets. As a result, the saturation level is highly dependent on the solution's temperature, as indicated by the solubility curve, as can be seen in figure 3.1.

In general, supersaturation happens simply when the salt concentration in the solution is higher than the solubility curve's concentration. In addition to heating the solution to 50 °C, stirring was used to speed up dissolving within the beaker using a magnetic stirrer. After that, the prepared solutions are either subjected to a pulsed

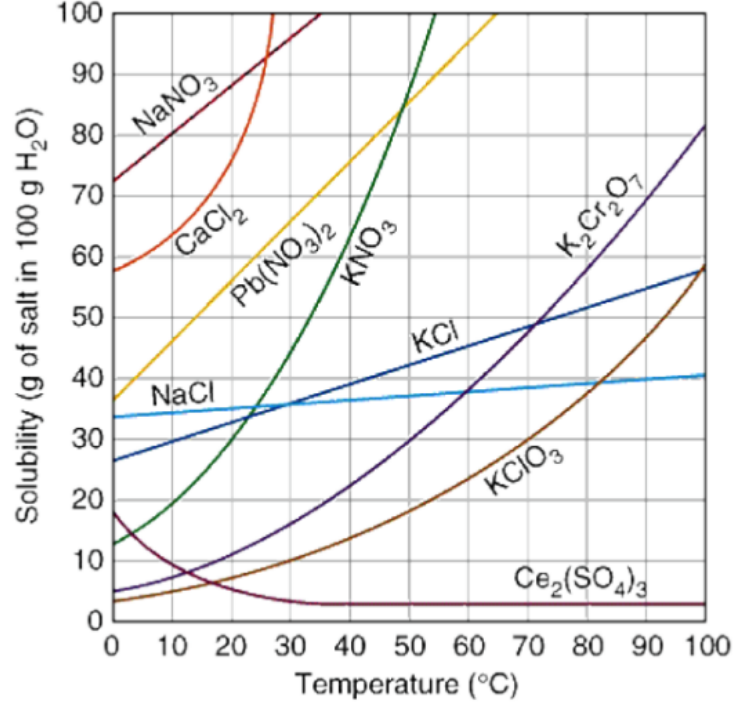


Figure 3.1: The solubility curve of some salts with temperature.

laser or allowed to crystallize naturally over an extended period of time without laser exposure.

3.2 Experimental Layouts

3.2.1 Laser Induced Crystallization Experimental Layout

Two types of lasers were used; the first laser was a Nd:YAG laser (Litron nano-series S 130-10) generating pulses at 532 nm wavelength with a pulse duration of 7 ns, beam size at focus spot of $2 \times 10^{-4} \text{ cm}^2$ and a repetition rate of 10 Hz. Laser pulses with varying energies (120, 130, 140, 150, and 160 mJ/pulse, which corresponds to laser peak power of 170, 186, 200, 214, and 229 GW/cm²) were vertically directed downward using a turning prism and focused into the center of the solution container

using a 75 mm plano-convex lens.

Figure 3.2 shows a schematic sketch of the main components of the setup to induce crystallization in aqueous KNO_3 solutions using nanosecond laser at 532 nm wavelength. The solution samples of 3.9 mL (3900 mm^3) volume of supersaturated aqueous solutions of potassium nitrate (KNO_3) were independently exposed to a single laser pulse and allowed to grow for different periods ranging from 1 to 7 minutes before harvesting.

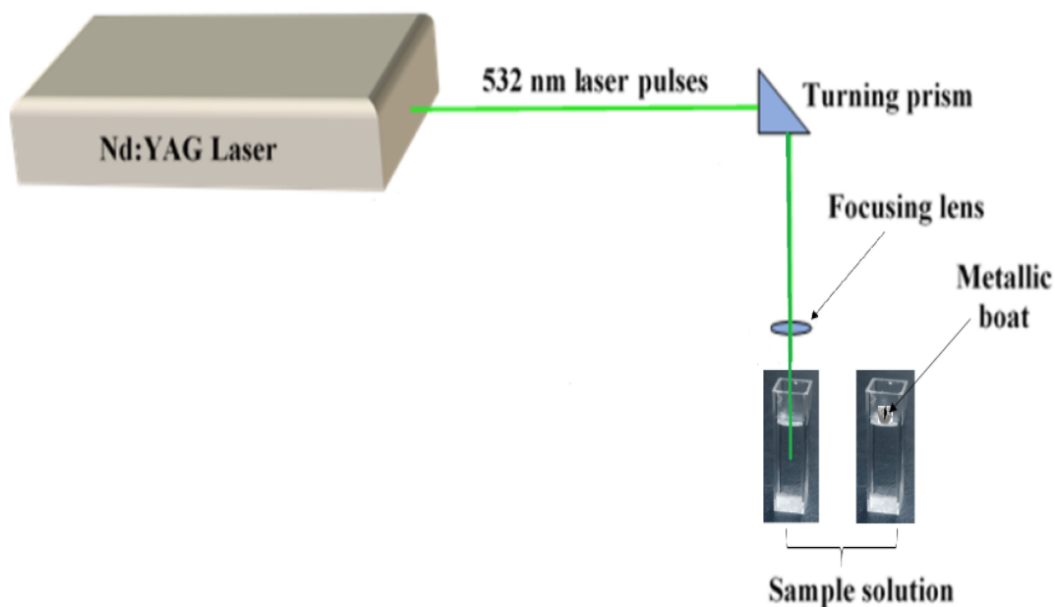


Figure 3.2: An illustration of the experimental setup used to induce crystallization in aqueous KNO_3 solutions using Nd:YAG laser.

Crystallization was achieved through two different experimental setups, leading to two distinct crystallization mechanisms. The first mechanism involved direct laser irradiation of the solution by focusing the laser in it, with a solution temperature of $23.20 \pm 0.05 \text{ }^\circ\text{C}$ measured by using an infrared thermometer and the laser beam size at the focal point of $2 \times 10^{-4} \text{ cm}^2$.

In the second setup, laser pulses hit a thin metallic boat floating on the solution surface, producing shockwaves that upon propagation could induce crystallization. Here, the laser beam diameter on the foil surface was roughly 3 mm to eliminate damage to the boat. The aluminum foil boat generated brief shockwaves upon laser impact, creating highly concentrated local areas within the solution that led to nucleation and crystal formation.

The produced crystals were allowed to grow for 1, 3, 5, and 7 minutes post-irradiation in each experimental setup to monitor their growth. Subsequently, the crystals were carefully harvested using filter paper and carefully allowed to dry. Then, placed on a cover glass on an Olympus IX73 inverted microscope to determine their size, shape, and size distribution.

Figure 3.3 shows a sketch of the main components of the setup to induce crystallization of KNO_3 using femtosecond laser.

Here, the laser used was a Ti:Sapphire laser that produced a 400 nm beam at a 76 MHz repetition rate. A 20 cm plano-convex lens was used to focus a laser beam with an energy of 10 nJ/pulse onto the center of the solution container after it had been vertically directed downward using a rotating prism. For varying lengths of time, ranging from 25 to 45 minutes, the solution samples of 100 mL volume of supersaturated aqueous solutions of potassium nitrate (KNO_3) were separately subjected to laser beam.

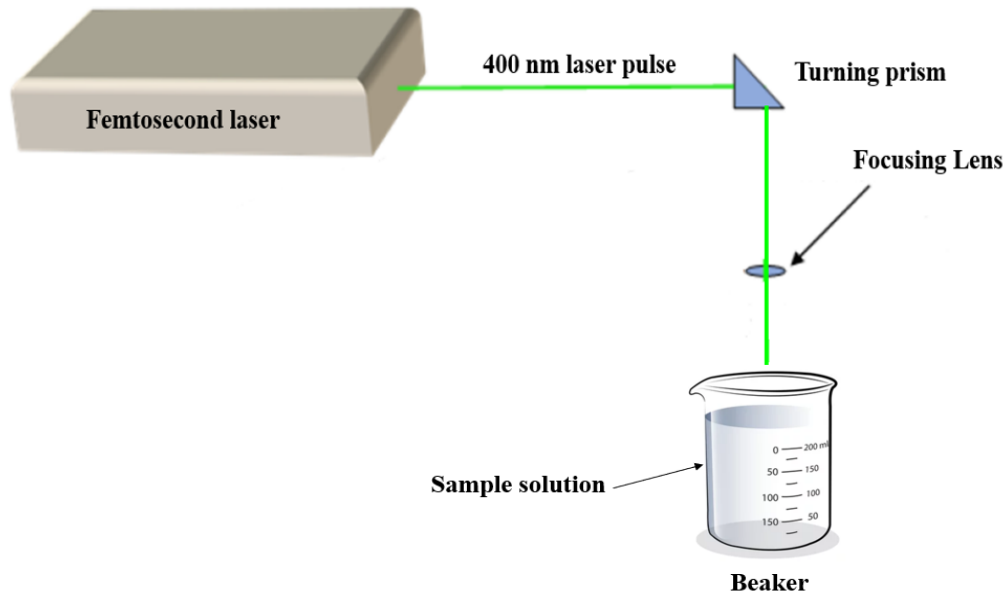


Figure 3.3: An illustration of the experimental setup used to induce crystallization in aqueous KNO_3 solutions using femtosecond laser.

3.2.2 Speed of Sound Experimental Layout

Speed of sound was measured to study the crystallization of KNO_3 in saturated and undersaturated solutions. By coupling an ultrasonic transducer to a Panametrics 5072 Pulser-Receiver 35 MHz on both sides of the cylinder, the speed of sound could be measured. The (Pulser/Receiver) was configured to measure the ultrasonic wave's speed as it passed through the solution. Using a Tektronix Digital Phosphor Oscilloscope (DPO-3054), the resultant signal was measured.

Figure 3.4 (a) shows a sketch diagram of the setup used to measure speed of sound in KNO_3 aqueous solutions. And Figure 3.4 (b) shows a photograph of the speed of sound measurement experiment.

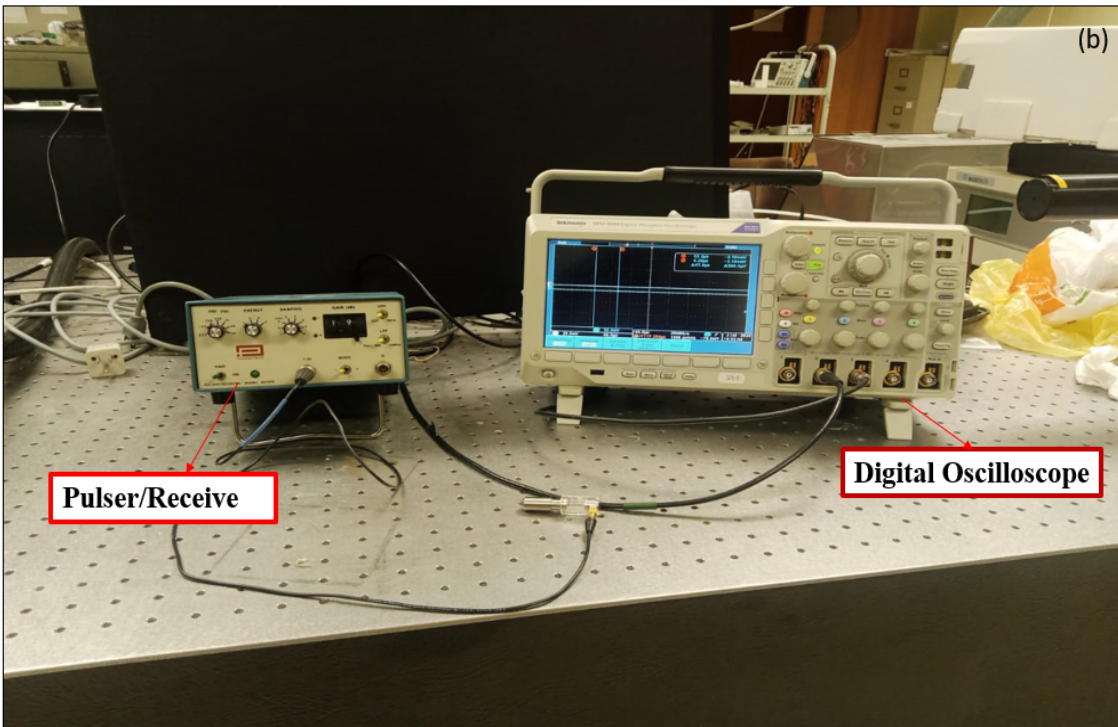
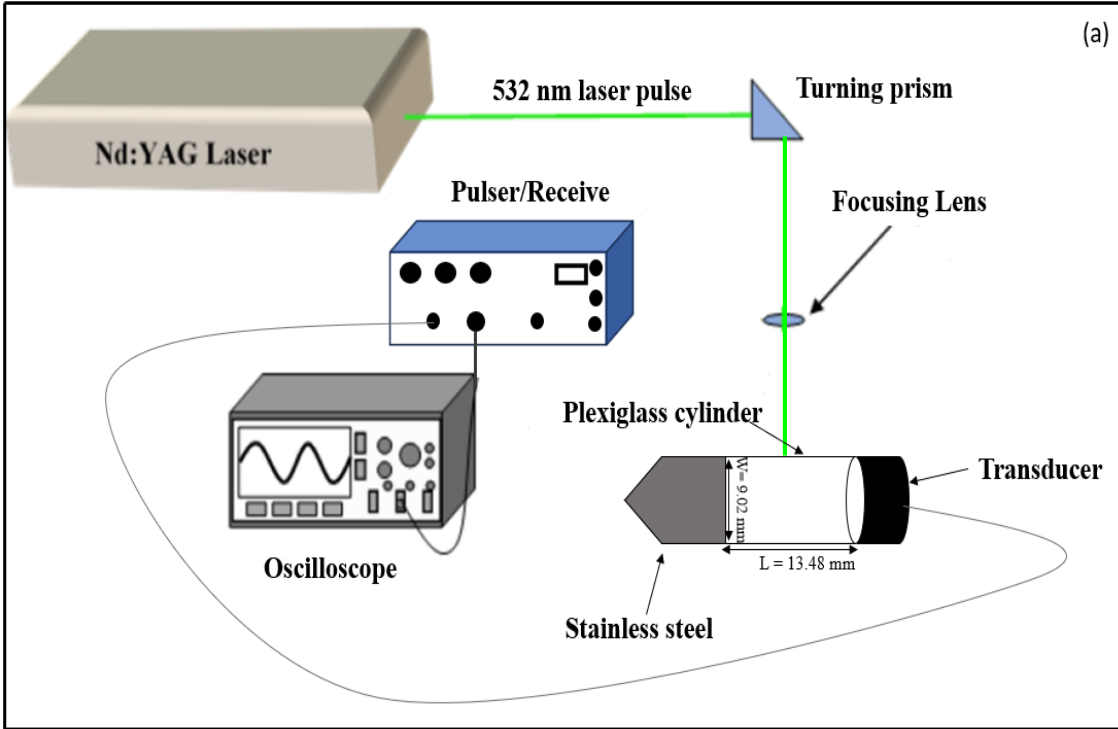


Figure 3.4: (a) A sketch of the setup used in the speed of sound measurement experiment. (b) A photograph of the speed of sound experiment apparatus.

3.3 Characterization Techniques

The primary purposes of the X-Ray Diffraction and Polarized Light Microscopy procedures were to supply much-needed details regarding the morphology and size distribution of the produced crystals.

3.3.1 X-Ray Diffraction (XRD)

In materials science, XRD is a technique used to assess the crystallographic structure of a material. It works by first subjecting a substance to incident X-rays, after which the intensities and scattering angles of the X-rays that escape the substance are measured. We employed XRD to investigate if the grown crystals contained any contaminants. This system of XRD shown in figure 3.5 which is located at Physics department, King Fahd University of Petroleum and Minerals (KFUPM).

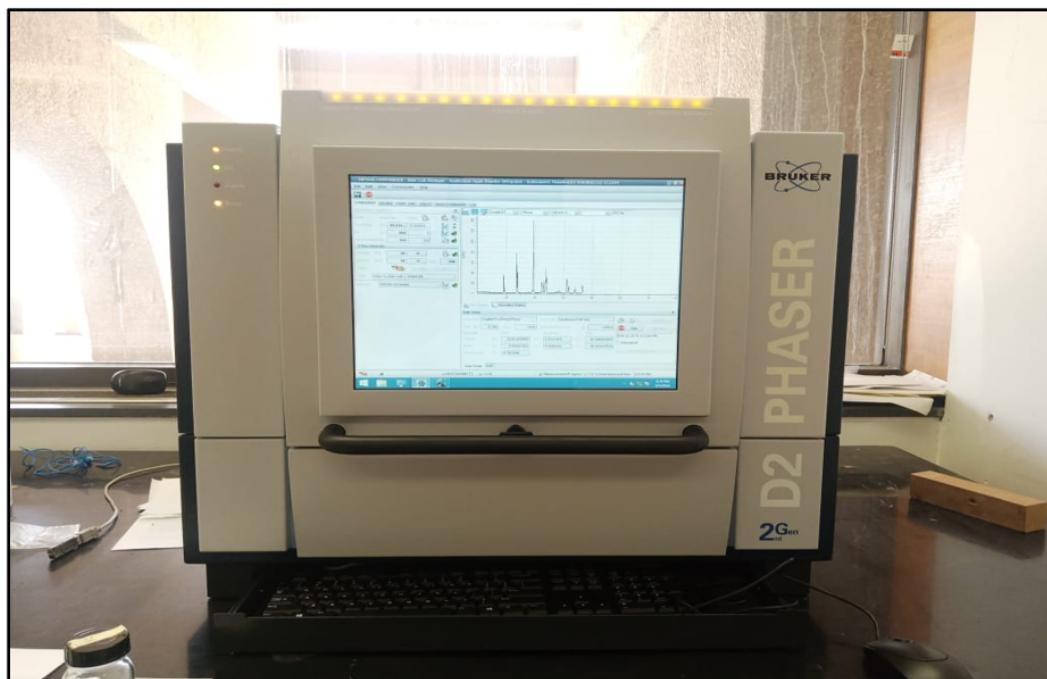


Figure 3.5: A photograph of the XRD utilized in this experiment.

3.3.2 Inverted Polarized Light Microscope (PLM)

The Olympus IX73 Inverted Optical Polarized Microscope, which has an objective magnification of up to 100x, was used as a reliable and economical method of determining the size and shape of produced crystals. Compared to FE-SEM technology, this method has substantially of less resolution. However, the crystals that were formed—particularly from the spontaneous crystallization—were big enough to be effectively characterized using this straightforward method. More significantly, and in contrast to a standard optical microscope, polarized light can provide pictures with much superior quality and can be used to describe transparent materials like crystals of nitrate salt. Figure 3.6 shows a photograph of PLM setup used to characterize grown crystals.

3.3.3 Field Emission Scanning Electron Microscope (FE-SEM)

The Field Emission Scanning Electron Microscope (FE-SEM) was used to examine the surface morphology of the nitrate salt crystals that were formed. The Tescan model Lyra-3 FE-SEM used in this experiment, which has a magnification of up to 10^6 , is photographed in Figure 3.7. This high-resolution microscopy system is located at Center of Excellence in Nanotechnology (CENT), King Fahd University of Petroleum and Minerals (KFUPM). The nitrate salt crystal samples were individually exposed to a concentrated electron beam and a stream of electrons in a high vacuum environment. Secondary electrons (SE), backscattered electrons (BSE), distinctive x-rays, and other

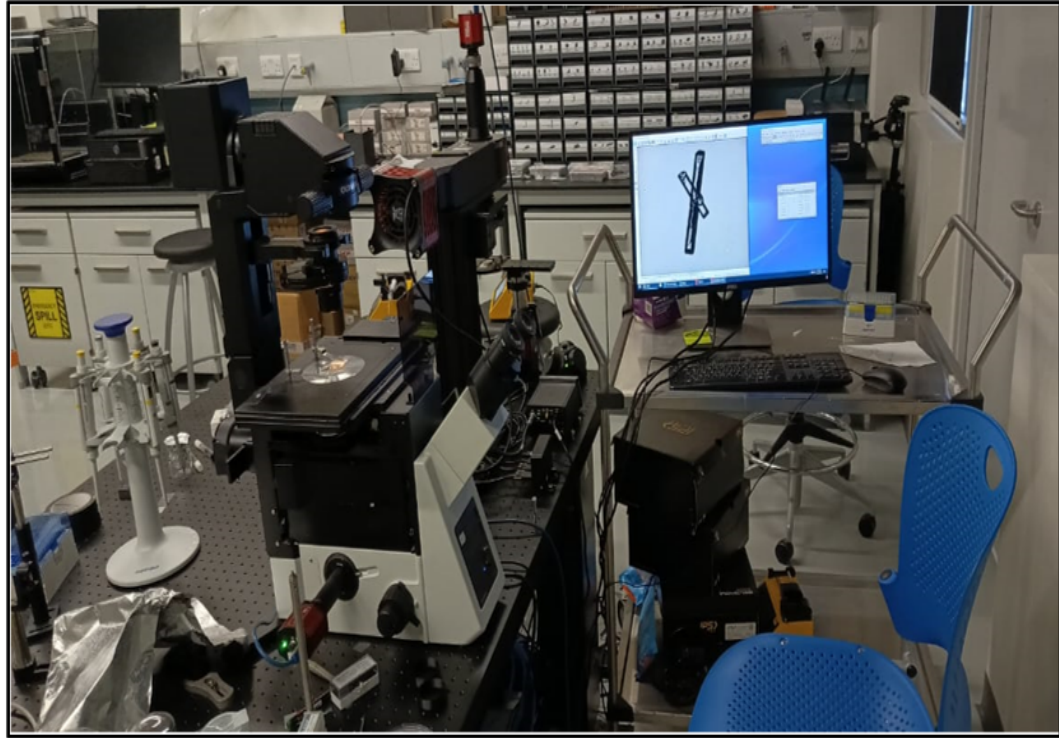


Figure 3.6: A photograph shows the PLM and the software used to analyze the crystal sizes in this experiment.

signals can theoretically be produced by the interaction of incident electrons with the sample. Nevertheless, secondary electrons are released from every location on the sample surface as a result of the incident electrons' inelastic collisions with it. These secondary electrons' velocity and angle are related to the object's surface structure. These secondary electrons are captured by a sensitive detector, which then generates an electrical signal that is amplified and processed to create a digital image that depicts the samples' microscopic microstructure.

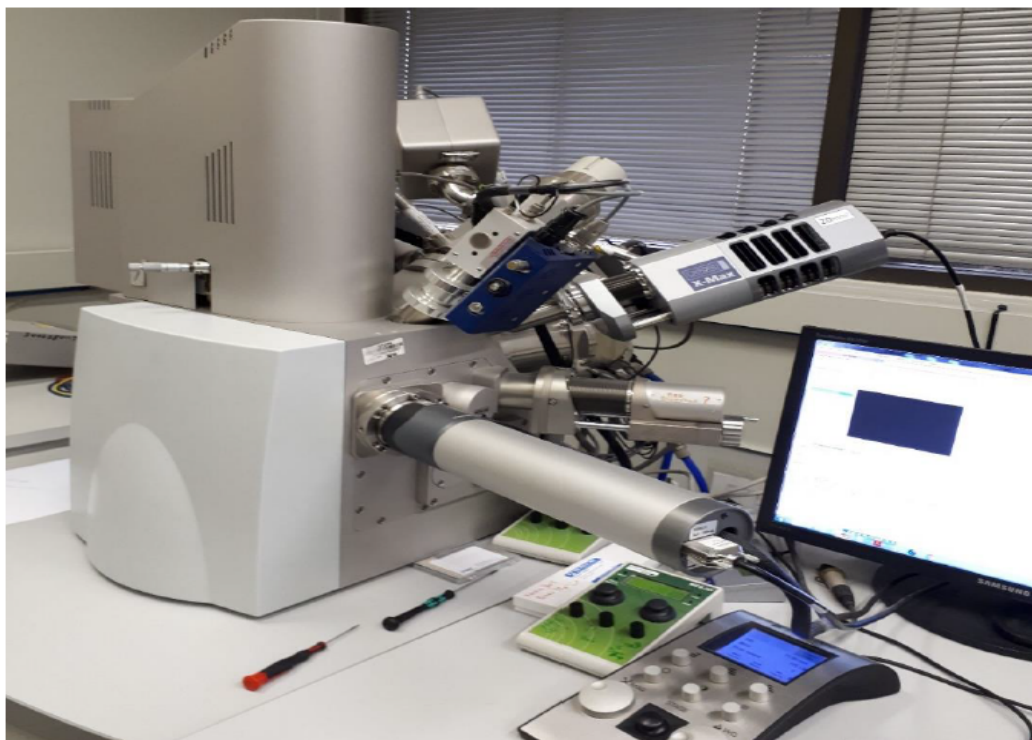


Figure 3.7: An image of the FE-SEM used in this experiment.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 XRD Results

Using a Bruker D2 PHASER diffractometer, which is using Copper as a radiation source, a polymorphic study of the potassium nitrate that was produced was performed. In order to get samples ready for powder X-ray diffraction, crystals were first taken out of the solution with forceps and allowed to dry. Using a mortar and pestle that had been cleaned after each sample was ground to prevent contamination, dried crystals were ground into a fine powder. The diffractometer was used to determine the diffracted X-ray intensity as a function of 2θ from 10° to 80° after a capillary tube containing the fine powder was inserted. The acquired data were contrasted with known potassium nitrate patterns.

Four different samples were analyzed by powder X-ray diffraction (pXRD), as can be seen in figure 4.1, showing that all of them were KNO_3 crystals. Crystal data were collected, showing that the crystal system for diffraction patterns in this study should be orthorhombic, the stable form at room temperature, with a space group of Pnma

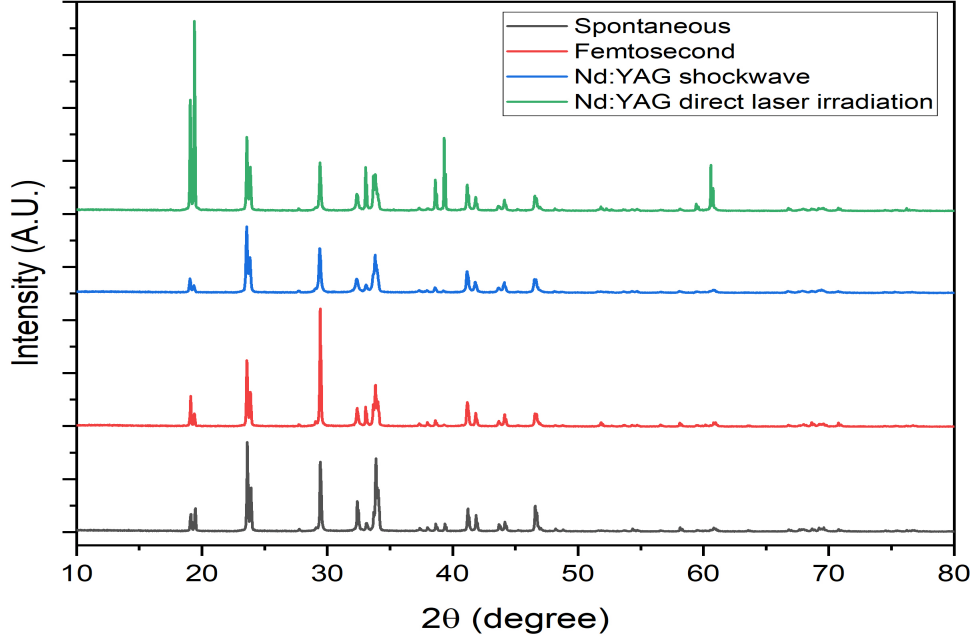


Figure 4.1: XRD patterns for spontaneously grown KNO_3 crystals (black), those created by femtosecond laser irradiation (red), shockwave-based Nd:YAG laser irradiation (blue), and direct Nd:YAG laser irradiation (green).

[37]. With the exception of direct laser irradiation based on Nd:YAG, we can see an extra peak at 2θ of 63° . This peak originates from the trigonal form of KNO_3 and is caused by the heat from the direct laser.

4.2 SEM Results

Figure 4.2 shows SEM image of KNO_3 crystals grown spontaneously without laser induction. The crystals shape was less regular than crystals grown using laser. Moreover, crystals were observed to be bulky and of average size length and width reach some centimeters.



Figure 4.2: SEM image of KNO_3 crystals grown conventionally without laser after 12 min [1].

Figure 4.3 shows KNO_3 crystals grown photochemically by direct laser irradiation. The crystals grown were observed to be more of regular shape and good quality compared to the spontaneous ones.

Figure 4.4 shows SEM image of KNO_3 crystals grown shockwave technique using the metallic boat layout. The crystals grown using this method are more regular and of sharper size distribution than crystals grown by direct laser induction.

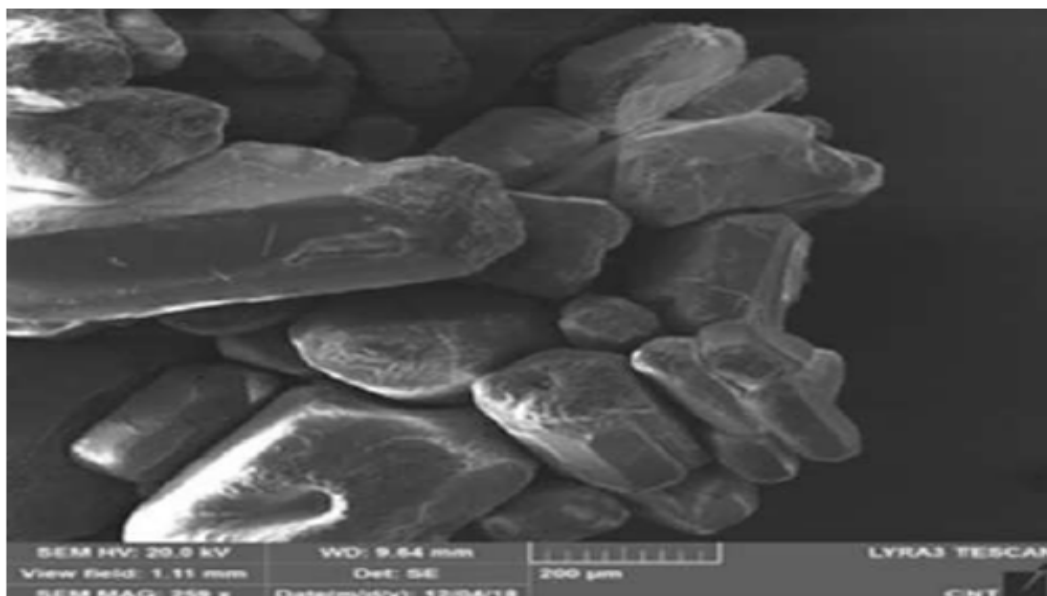


Figure 4.3: SEM image of KNO₃ crystals grown by direct laser irradiation after 12 min [1].

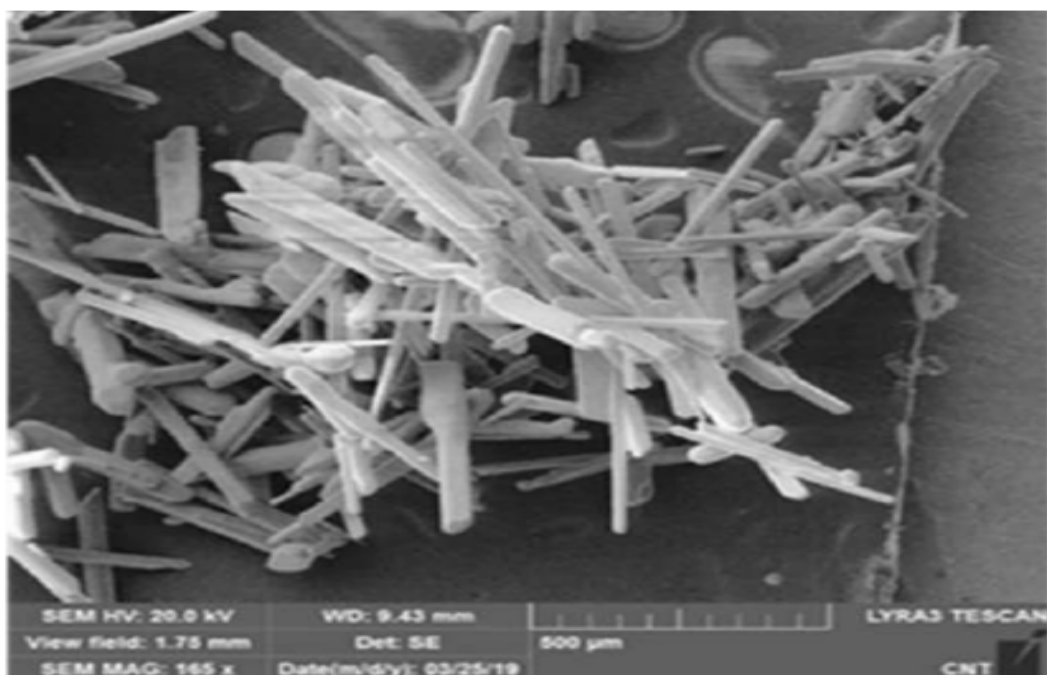


Figure 4.4: SEM image of KNO₃ crystals grown by shockwave laser irradiation after 10 min [1].

4.3 Mechanisms of Crystallization by Different Techniques

The solution of potassium nitrate salt at the same saturation level used in conventional crystallization was exposed to a focused beam of short laser pulses (MaiTai-Spectra Physics) at a wavelength of 800 nm with energy per pulse of 10 nJ which corresponds to a peak power density of 10 GW/cm^2 , the width of the laser pulse was 100 fs, and a repetition rate of 85 MHz for a period of 30 minutes in order to investigate the impact of the laser on crystallization by focusing the laser beam using a 75-mm focal lens. The resulting crystals from laser-induced nucleation were completely different from those made by spontaneous crystallization, even though supersaturated solutions may crystallize without any induced perturbations. Figure 4.5 shows photographs of KNO_3 crystals produced spontaneously after 50 minutes, as at this time the crystals start to appear (right) and laser-induced crystals after 30 minutes of irradiation (left) for solutions at 1.32 ± 0.05 saturation levels. After 30-minute exposure, the laser-exposed sample was captured by a smartphone camera, and the control sample, which was not exposed by the laser, was also captured after 50 minutes, as we can see in figure 4.5. The size of the crystals produced by pulsed laser exposure is significantly less than that of crystals generated by normal crystallization or ablation, which suggests that there are several nucleation sites in the solution. One possibility could be that the laser pulses started the nucleation sites early before they grew into larger crystals. The nucleation rate is faster than that of the spontaneous crystallization, as demonstrated by the large number of crystals created by laser-induced crystallization. This might be

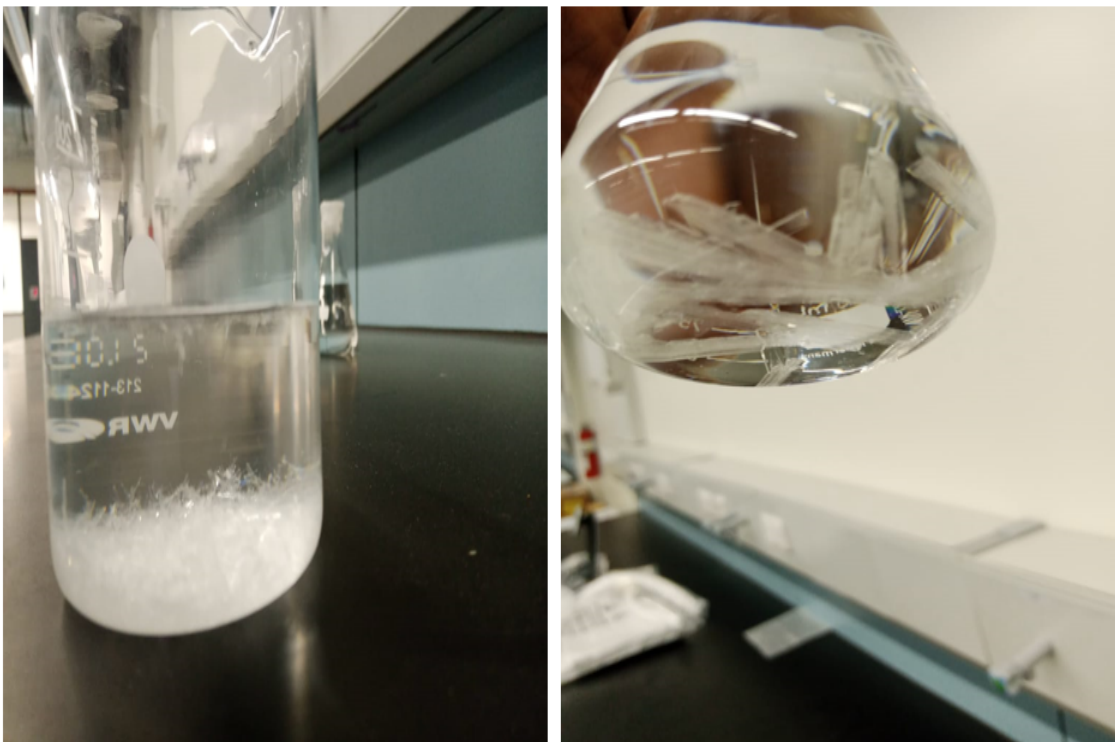


Figure 4.5: KNO_3 crystals produced by laser irradiation (left), and crystals produced spontaneously (right).

because of ablation. The solutes in the solution are quickly depleted by the crystals' development, which causes nucleation to stop later in the crystallization process. As a result, most crystals reach roughly the same size. In contrast, the nucleation rate is slower during conventional crystallization, causing the clusters to nucleate at different times because to the extended duration of the driving force caused by supersaturation. Because of this, conventional crystallization only creates crystals of varying sizes in certain locations.

4.3.1 Laser-Induced Crystallization of KNO_3 using Femtosecond Laser Pulses

A 400 nm focused laser beam with an energy of 10 nJ/pulse, a 76 MHz repetition rate, a pulse duration of 200 fs, and a 20 cm focal lens was used to irradiate a solution of potassium nitrate salts at the same saturation level used in conventional crystallization over a range of exposure times in order to investigate the impact of the Ti:Sapphire femtosecond laser on crystallization. Solution samples of 100 mL volume of supersaturated aqueous solutions of potassium nitrate (KNO_3) were individually exposed to a continuous laser beam for varied periods of time, ranging from 25 to 45 minutes.

Table 4.1: Illustrates the mass of the crystals produced after laser irradiation.

Time (minutes)	Mass (g)
25	0.3925
30	1.0883
35	4.1945
45	10.2524

The mass of the produced crystals at various laser irradiation times—25, 30, 35, and 45 minutes—is displayed in Figure 4.6. The equation displays the fitting parameters, $K_0 = 97.8$, $K_1 = -9.1$, and $K_3 = 0.03$. It was best fitted to a 4 degree polynomial.

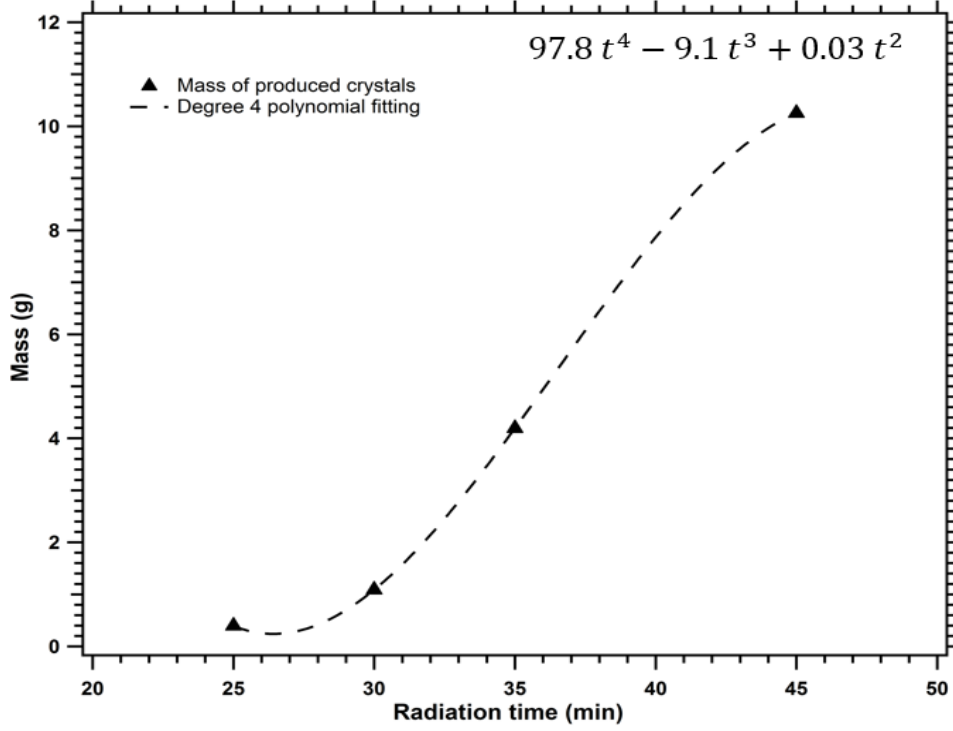


Figure 4.6: Demonstrate the crystal's mass that was formed after 25 minutes, 30 minutes, 35 minutes, and 45 minutes of laser irradiation.

As we can see in figure 4.7 (a), the number and size of the crystals were small at 25 irradiation time, and as we increase the irradiation time, both size and number increase, as we can see in figures 4.7 (b), (c), and (d). Figure 4.7 displays an image of the crystals produced using a femtosecond laser.

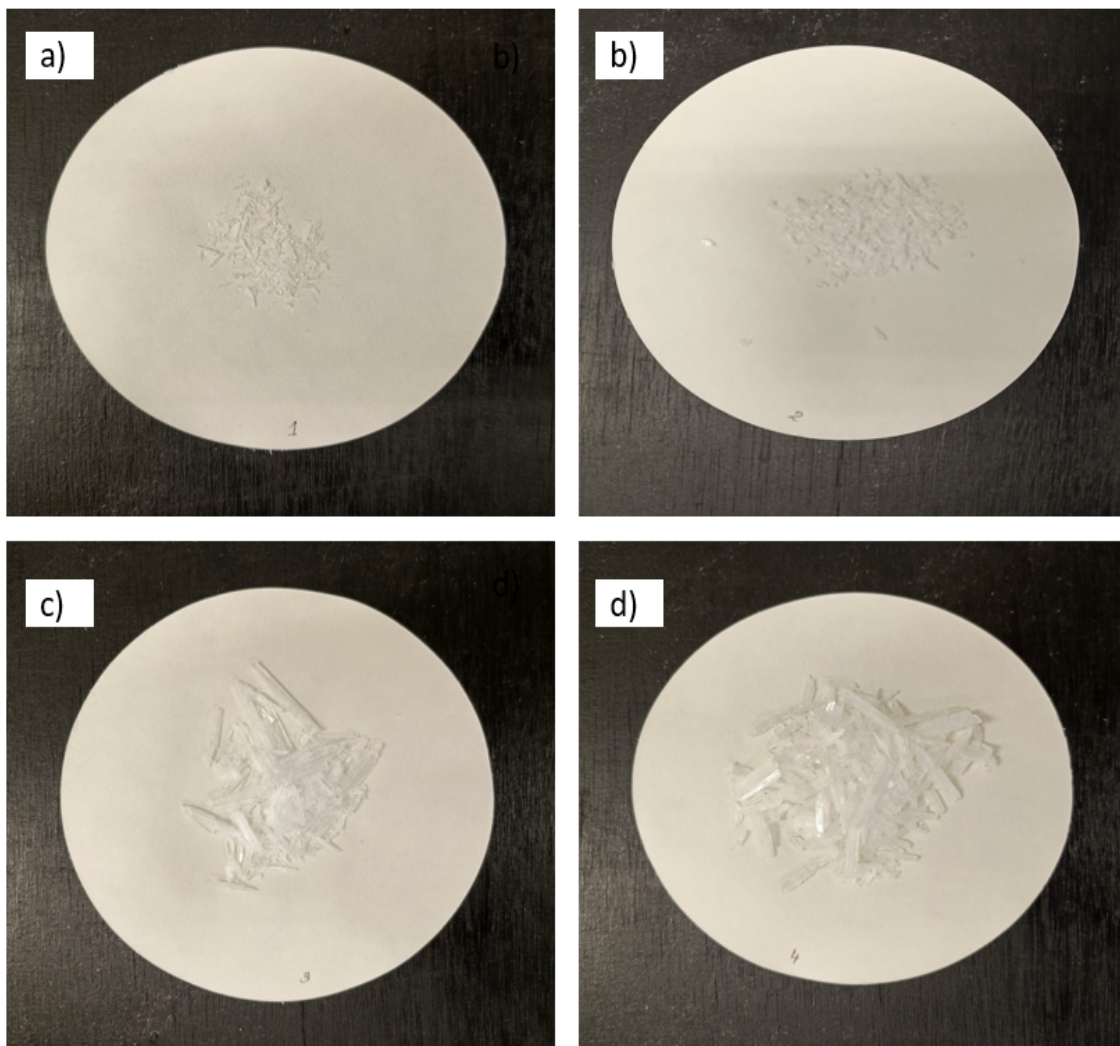


Figure 4.7: Photographs demonstrate the crystals that were formed after (a) 25 minutes, (b) 30 minutes, (c) 35 minutes, and (d) 45 minutes.

4.3.2 Laser-Induced Crystallization of KNO_3 using single pulse of Nanosecond laser

In order to study the effect of the single pulse of Nd:YAG laser on crystallization, the solution of nitrate salts at the same saturation level used in conventional crystallization

was irradiated by the focused laser pulses of 532 nm with varying energies of (120, 130, 140, 150, and 160 mJ/pulse, which corresponds to laser peak power of 170, 186, 200, 214, and 229 GW/cm²) and 7 ns pulse duration with a 75 mm focal lens over different exposure times. Figure 4.8 shows some of characterized crystals using IX73 inverted polarized microscope.

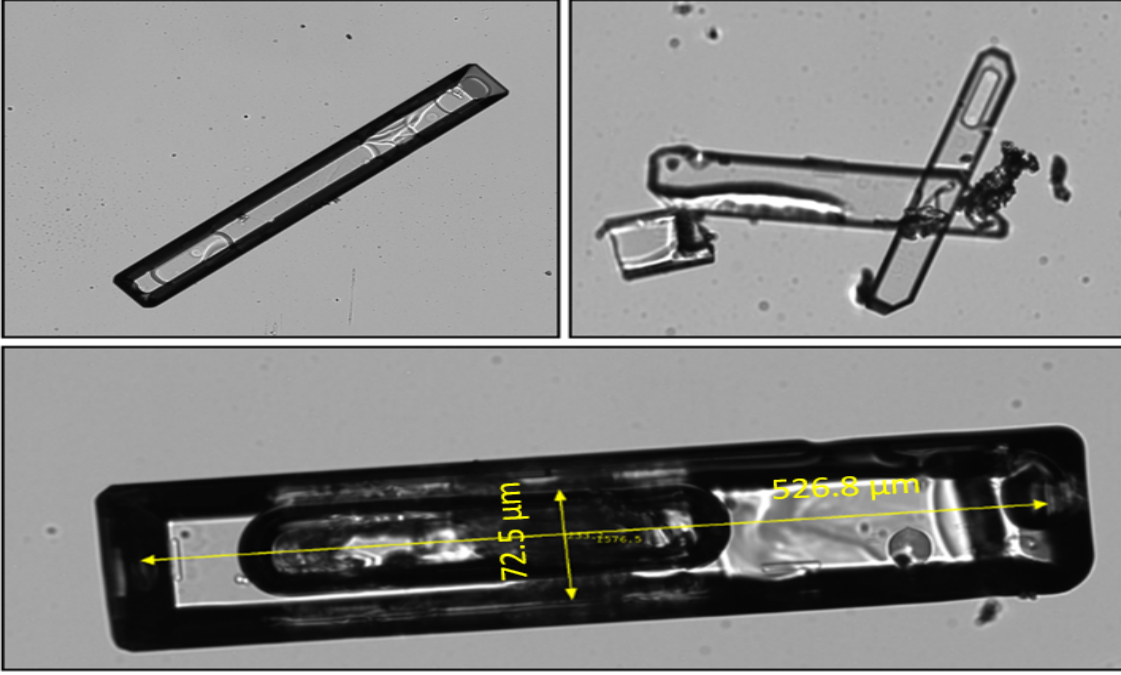


Figure 4.8: Images showing KNO₃ crystals under Polarized Light Microscope.

4.3.3 Direct laser irradiation technique

In this technique, the Nd:YAG laser was used with direct irradiation of the samples. Figure 4.9 (a) shows the length distribution of 100 crystals of KNO₃ grown photochemically of laser energy of 120 mJ using a single pulse of a nanosecond laser. It can be seen that at time elapse of 1 minute, the most probable value for the number of crystals occurs at length 23.9 μm , and figures 4.9 (b) and (c) show that the crystal

length has shefted to $82.5 \mu\text{m}$ and $249.5 \mu\text{m}$ respectively. While, in figure 4.9 (d) the crystals mean length grow to $367.9 \mu\text{m}$.

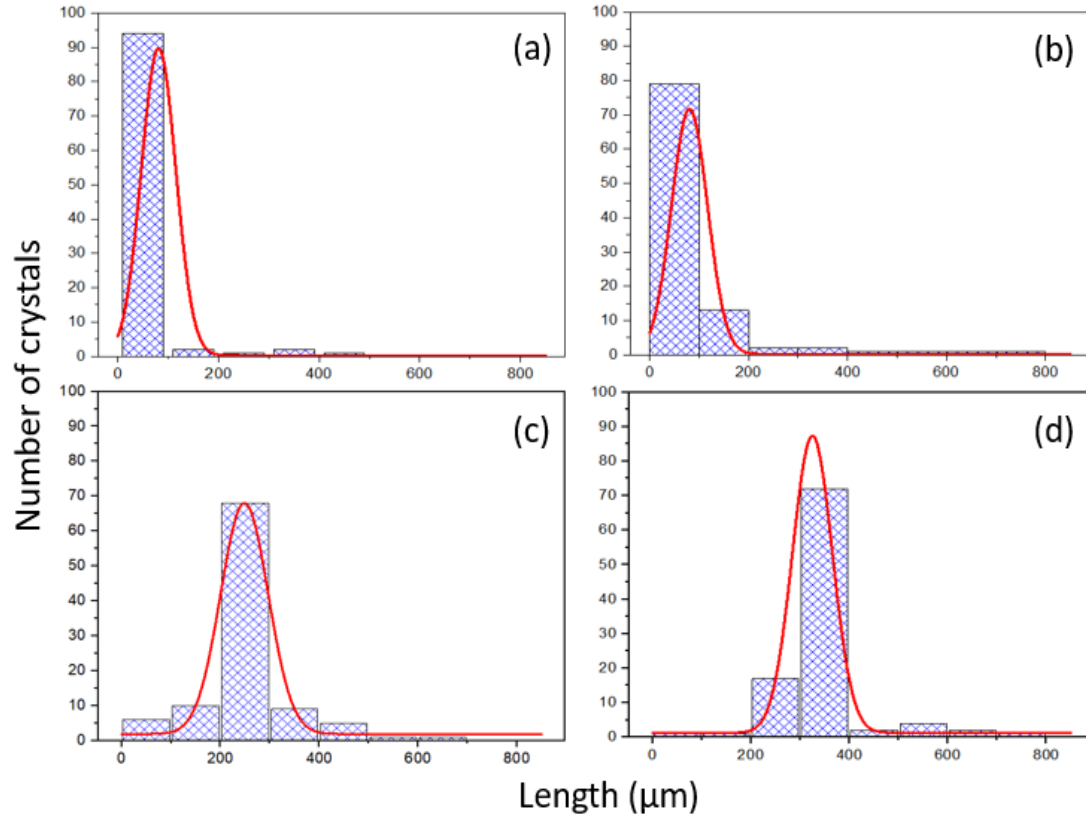


Figure 4.9: Length distributions of KNO_3 crystals grown by direct laser technique at laser energy 120 mJ at (a) 1 min, (b) 3 min, (c) 5 min, and (d) 7 min.

Figure 4.10 (a) shows the width distribution of 100 produced crystals of KNO_3 grown photochemically at energy 120 mJ. It can be seen that at 1 minute time elapse, the most probable value for the number of crystals occurs at width $10.5 \mu\text{m}$. Figures 4.10 (b) and (c) show that the crystal width has shefted to $45.4 \mu\text{m}$ and $67.7 \mu\text{m}$ respectively. While, in figure 4.10 (d) the crystals mean width grow to $71.2 \mu\text{m}$.

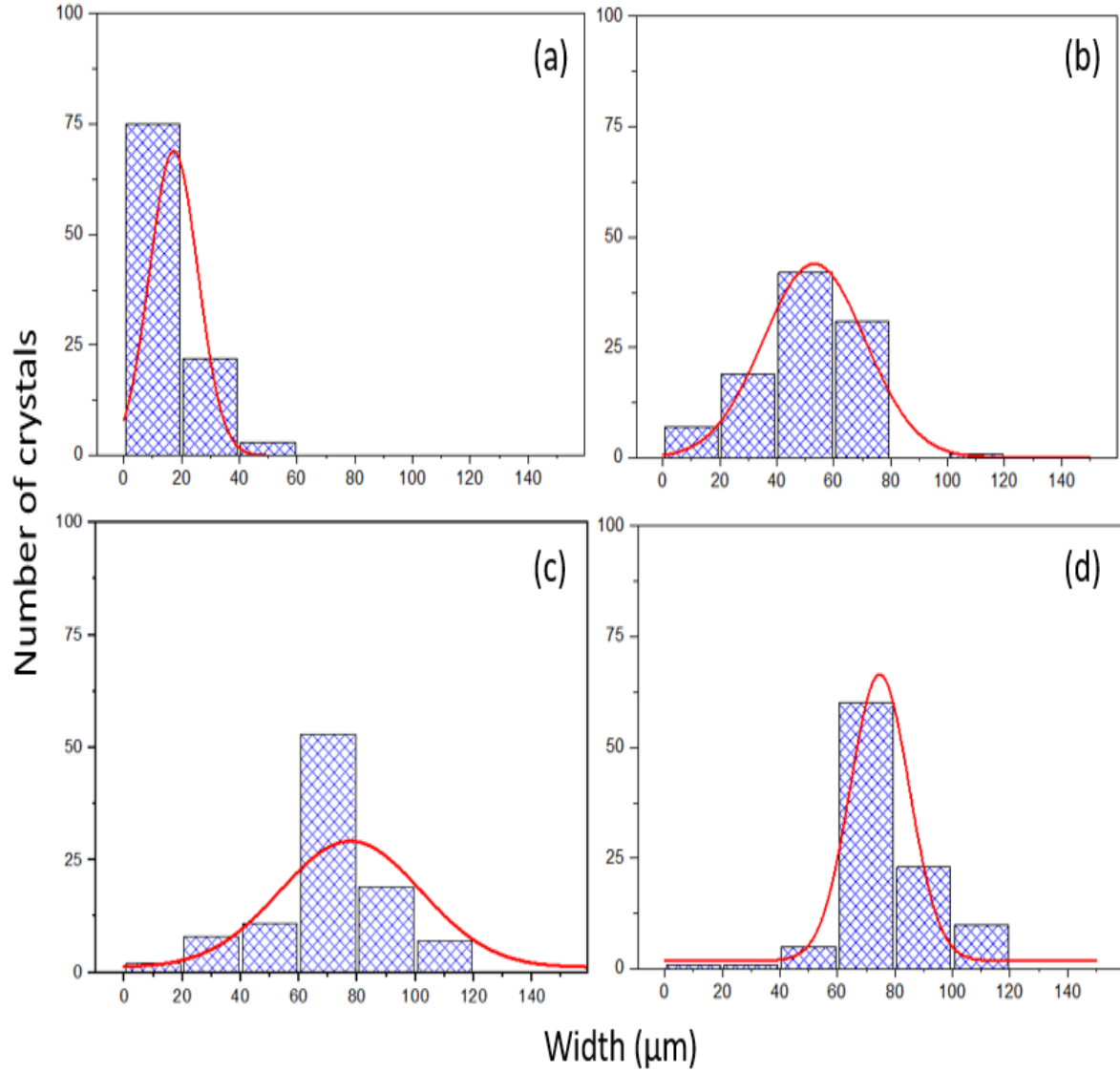


Figure 4.10: Width distributions of KNO_3 crystals grown by direct laser irradiation technique at energy level 120 mJ at (a) 1 min, (b) 3 min, (c) 5 min and (d) 7 min.

The length distribution of 100 generated crystals of KNO_3 formed photochemically at energy 130 mJ is displayed in figure 4.11. Figure 4.11 (b) and (c) demonstrate that the crystal length had grown to 203.8 μm and 425.0 μm , respectively, and that at 1 minute time elapse, the most likely value for the number of crystals occurs at length

98.4 μm as can be seen in figure 4.11 (a). In contrast, the mean length of the crystals increases to 493.7 μm in figure 4.11 (d) after 7 minutes time elapse.

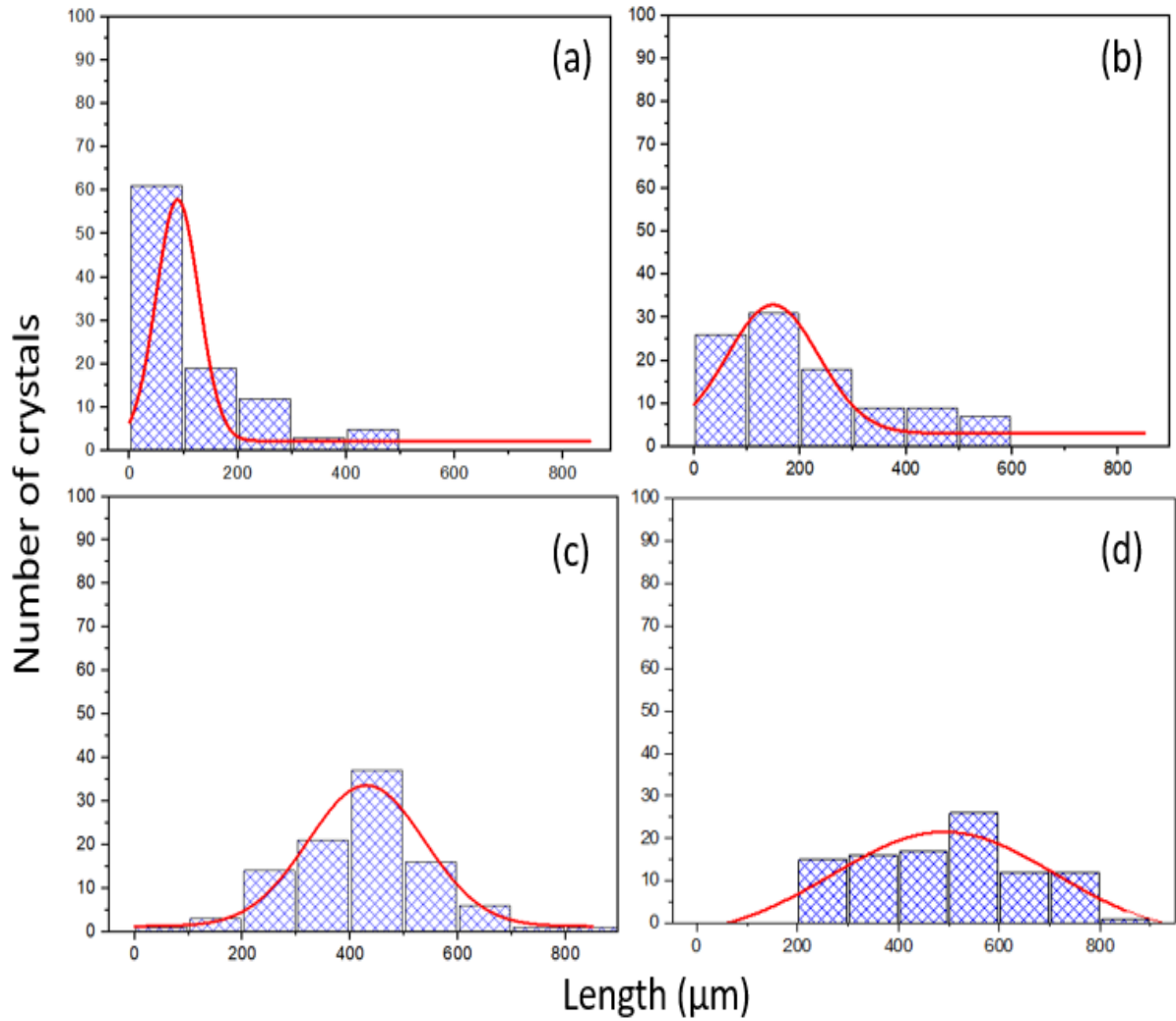


Figure 4.11: Length distributions of KNO_3 crystals grown by direct laser irradiation technique at energy level 130 mJ at (a) 1 min, (b) 3 min, (c) 5 min, and (d) 7 min.

The width distribution of the 100 generated crystals of KNO_3 formed photochemically at energy 130 mJ is displayed in Figure 4.12. Figure 4.12 (b) and (c) demonstrate that the crystal width had shefted to 50.5 μm and 59.5 μm , at time 3 and 5 minutes, respectively, and that at 1 minute time elapse, the most likely value for the number of

crystals occurs at width $33.9 \mu\text{m}$. In contrast, the mean width of the crystals increases to $72.6 \mu\text{m}$ in figure 4.12 (d) after 7 minutes.

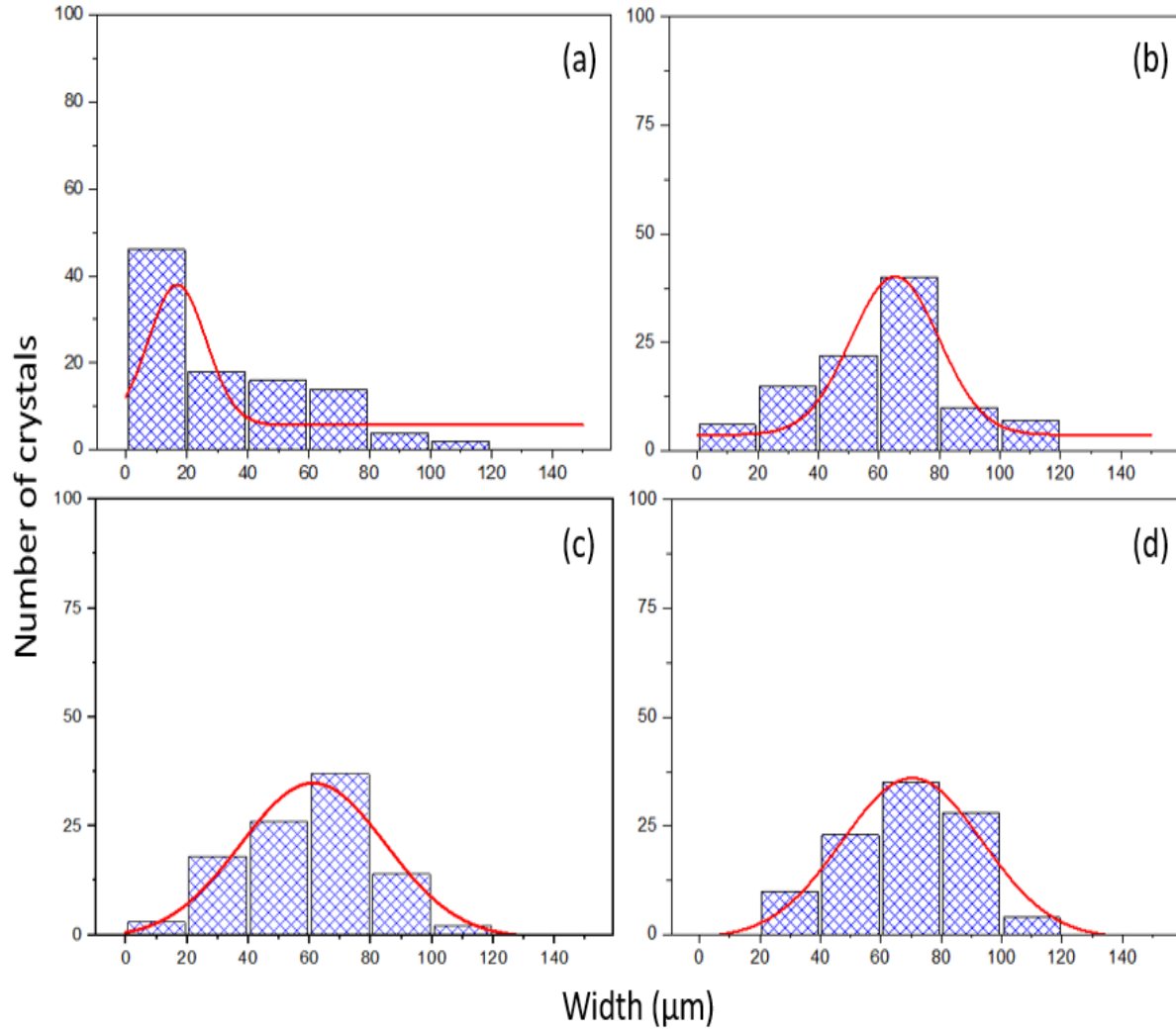


Figure 4.12: Width distributions of KNO_3 crystals grown by direct laser irradiation technique at energy level 130 mJ at (a) 1 min, (b) 3 min, (c) 5 min and (f) 7 min.

The majority of the crystals had either broken or stuck to one another after five minutes, which is made it challenging to estimate their lengths precisely at energy equal to or higher than 140 mJ. We therefore take crystal measurements at 0.5, 1, 2, and 3 minutes. Figure 4.13 shows the length distribution of 100 KNO_3 crystals that

were produced photochemically at an energy of 140 mJ. The crystal length had shifted to $191.8 \mu\text{m}$ and $233.7 \mu\text{m}$, respectively, as shown in figure 4.13 (b) and (c). At 30 seconds time elapse, the length $63.7 \mu\text{m}$ is the most plausible value for the number of crystals. Conversely, in figure 4.13 (d), the average crystal length rises to $297.5 \mu\text{m}$.

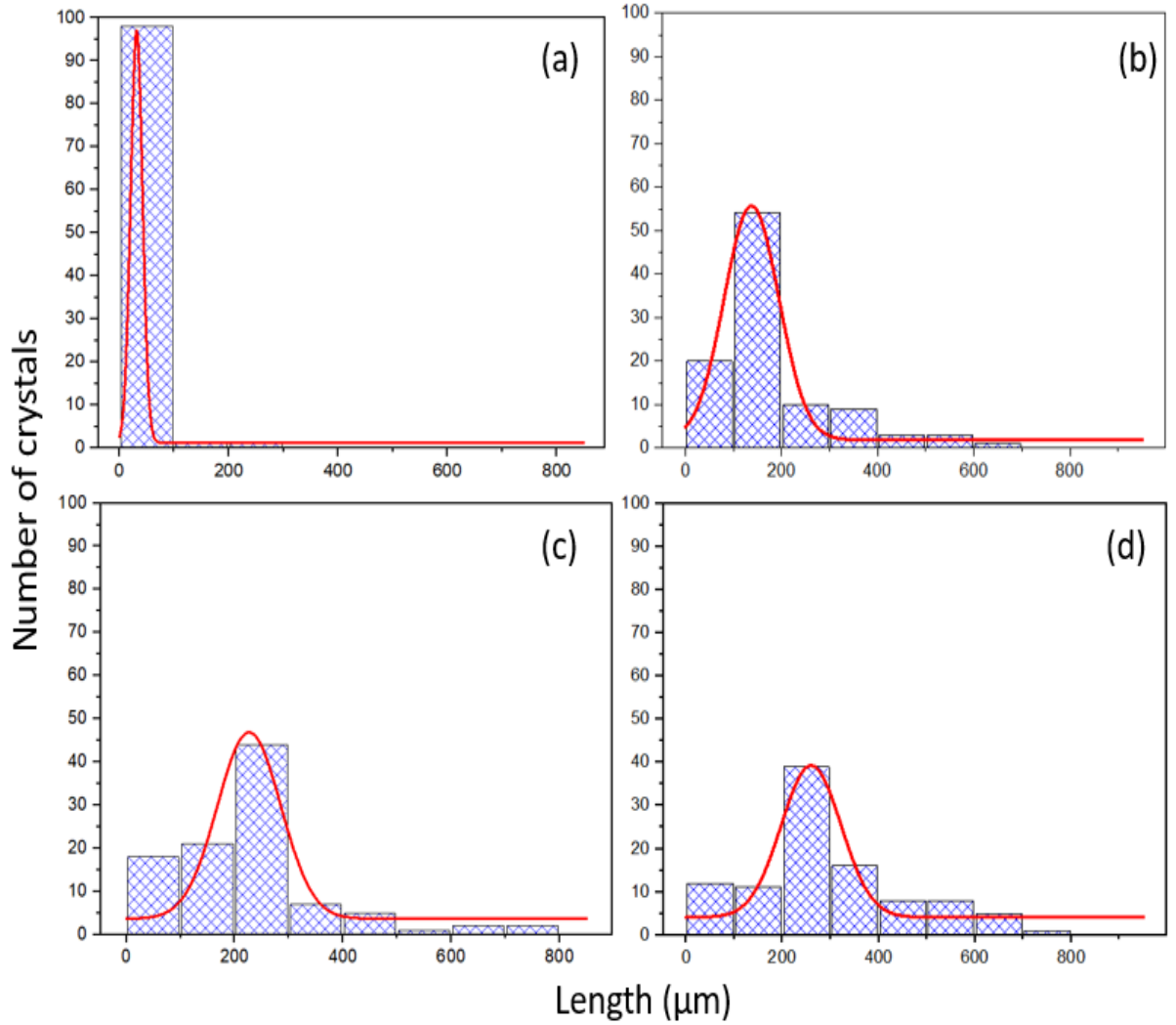


Figure 4.13: Length distributions of KNO_3 crystals grown by direct laser irradiation technique at energy level 140 mJ at (a) 30 sec, (b) 1 min, (b) 2 min and (d) 3 min.

Figure 4.14 shows the width distribution of the KNO_3 crystals that were produced photochemically at an energy of 140 mJ. The crystal width had shifted to $74.7 \mu\text{m}$

and $75.8 \mu\text{m}$, respectively, as shown in figure 4.14 (b) and (c). At 1 minute, the width of $41.4 \mu\text{m}$ is the most plausible value for the number of crystals. In contrast, in figure 4.14 (d), the average crystal width increases to $80.2 \mu\text{m}$ after a 7-minute time elapse.

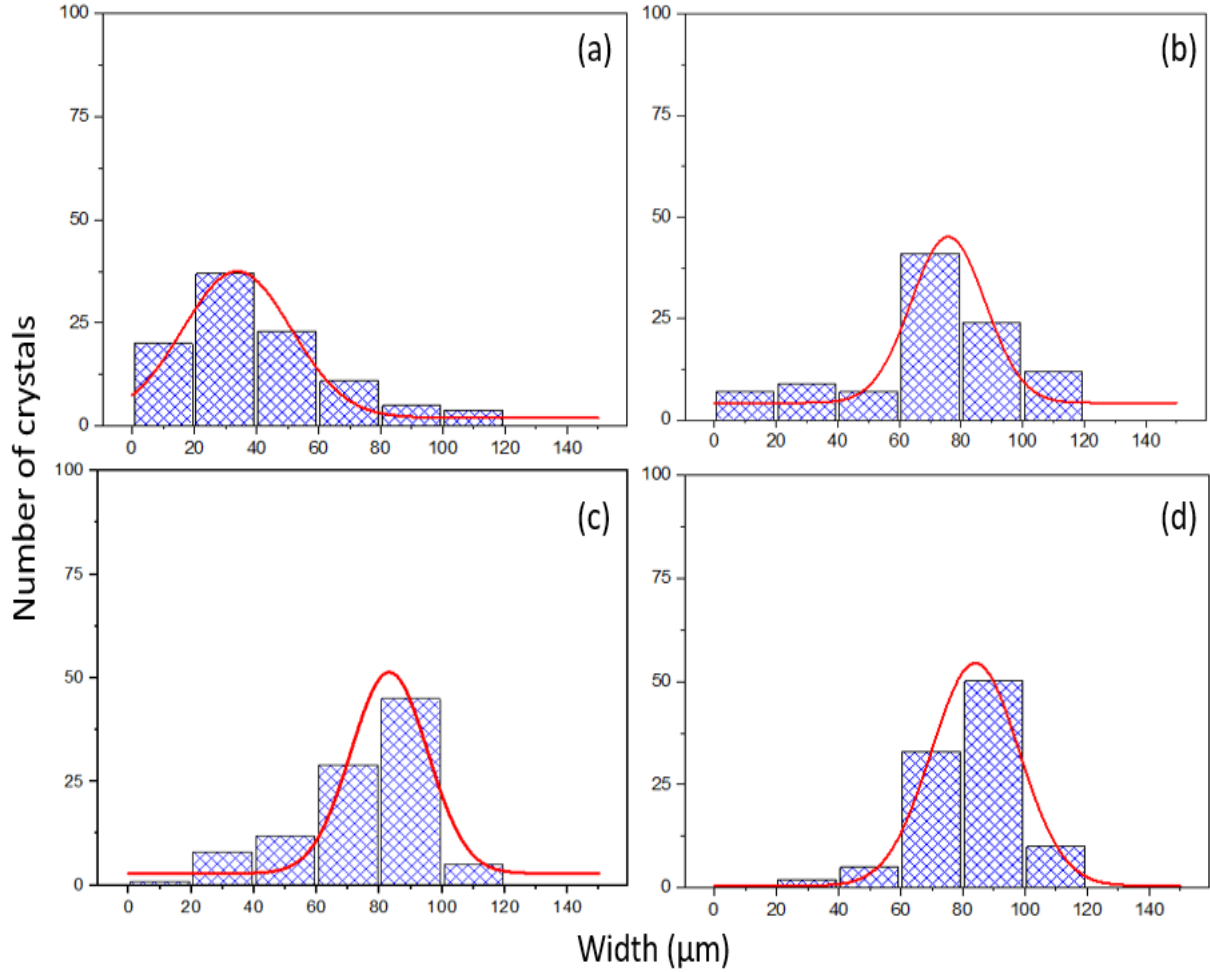


Figure 4.14: Width distributions of KNO_3 crystals grown by direct laser irradiation technique at energy 140 mJ at (a) 1 min, (b) 3 min, (c) 5 min and (d) 7 min.

Similarly, it was difficult to determine the exact lengths of the crystals at this energy because most of the crystals had either fractured or adhered to one another after five minutes. As a result, we measure crystals at 0.5, 1, 2, and 3 minutes time elapse. The length distribution of 100 KNO_3 crystals that were created photochemically at

an energy of 150 mJ is displayed in Figure 4.15. As seen in figure 4.15 (b) and (c), the crystal length had increased to 355.8 μm and 404.9 μm , respectively. The length of 192.2 μm is the most likely number of crystals at 30 seconds. On the other hand, the average crystal length increases to 737.1 μm in figure 4.15 (d).

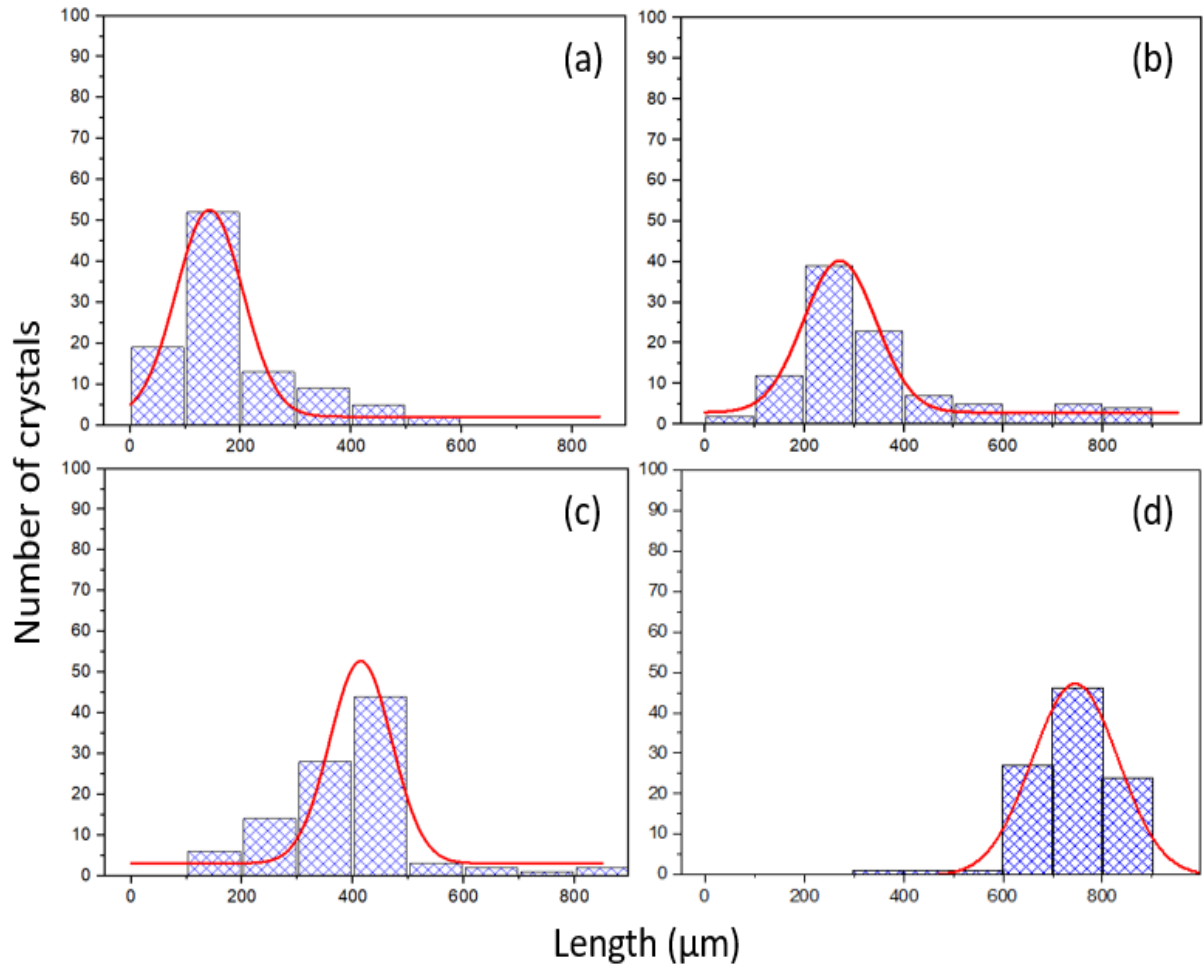


Figure 4.15: Length distributions of KNO_3 crystals grown by direct laser irradiation technique at energy level 150 mJ at (a) 30 sec, (b) 1 min, (c) 2 min and (h) 3 min.

The width distribution of KNO_3 crystals generated photochemically at an energy of 150 mJ is displayed in Figure 4.16. In Figure 4.16 (b) and (c), the crystal width had shefted to 102.2 μm and 104.9 μm , respectively. The most likely width for the

number of crystals at 1 minute is $90.1 \mu\text{m}$. In comparison, the average crystal width rises to $100.0 \mu\text{m}$ in figure 4.16 (d).

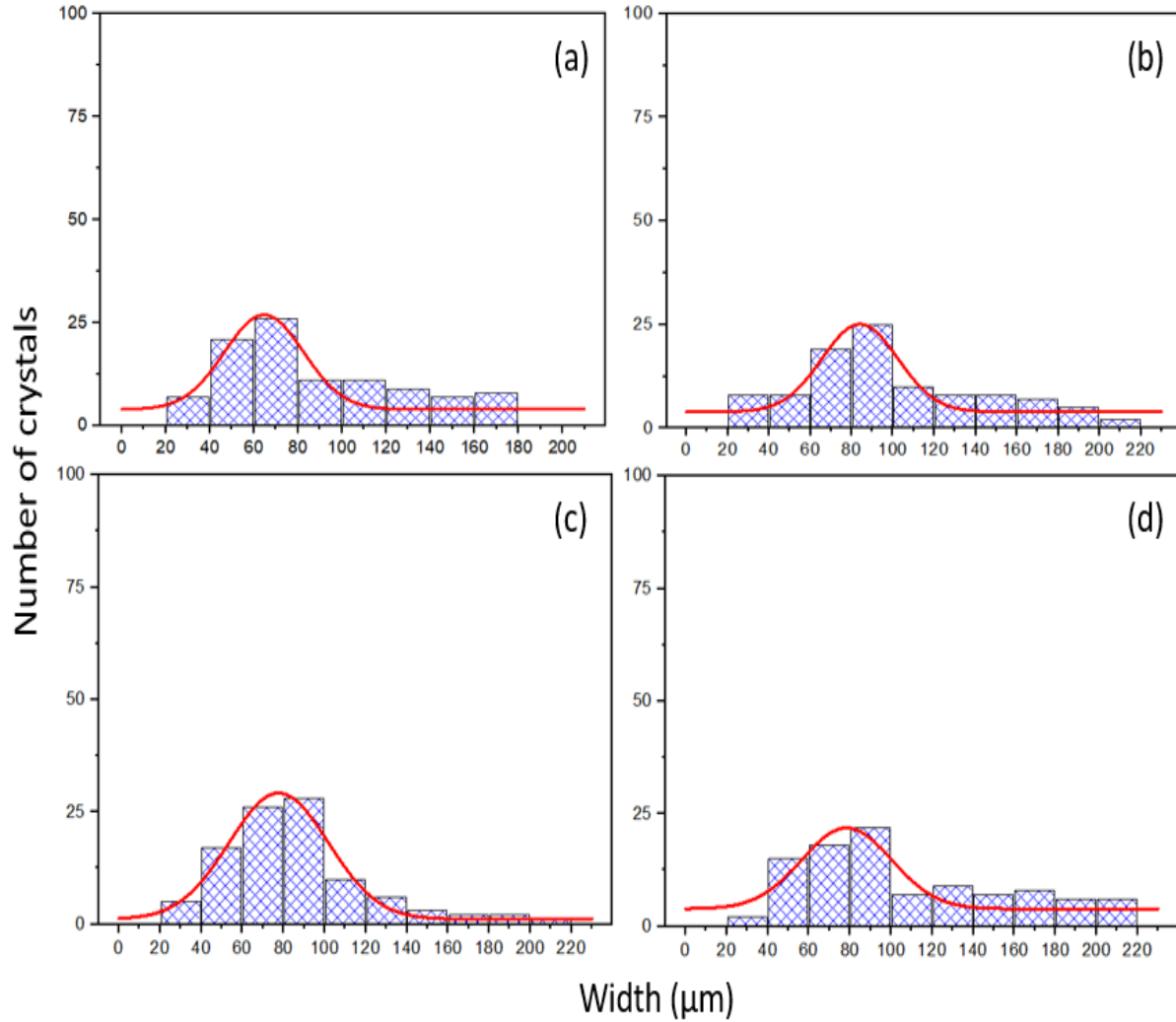


Figure 4.16: Width distributions of KNO_3 crystals grown by direct laser irradiation technique at energy level 150 mJ at (a) 1 min, (b) 3 min, (c) 5 min, and (d) 7 min.

4.3.4 Shockwave Technique

In this technique, the Nd:YAG laser was used with a mettalic boat flow over the sample solution to generate a shockwave. Figure 4.17 (a) shows the length distribution of 100

produced crystals of KNO_3 grown by shockwave at energy 120 mJ. It can be seen that at 1 minute time elapse, the most probable value for the number of crystals occurs at length $30.5 \mu\text{m}$, and in figures 4.17 (b) and (c) show that the crystal length has grown to $129 \mu\text{m}$ and $233.3 \mu\text{m}$ respectively. While, in figure 4.17 (d) the crystals mean length grow to $310.1 \mu\text{m}$.

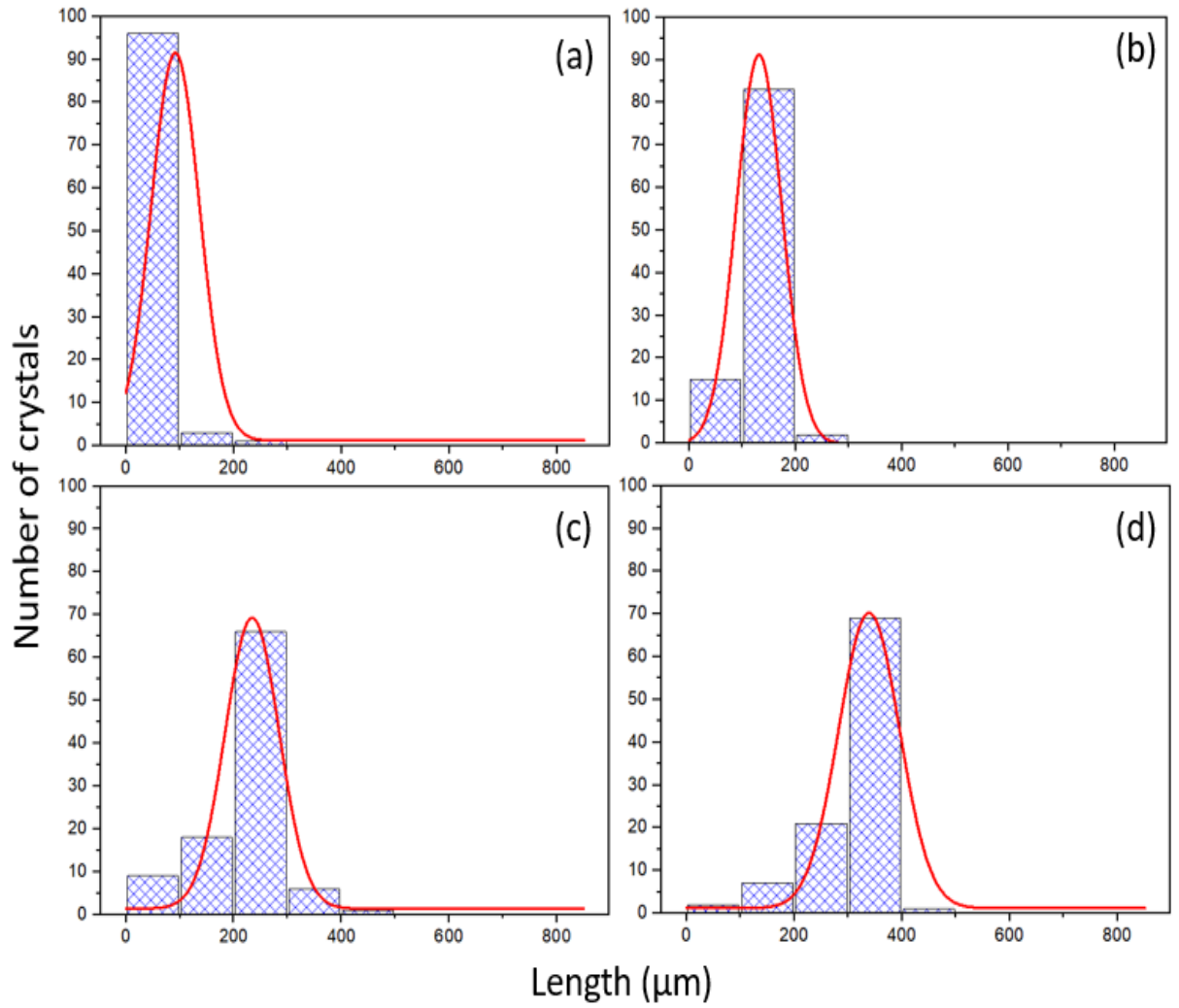


Figure 4.17: Length distributions of KNO_3 crystals grown by non-photochemical (shockwave laser) technique at energy level 120 mJ at (a) 1 min, (b) 3 min, (c) 5 min, and (d) 7 min.

Figure 4.18 (a) shows the width distribution of 100 produced crystals of KNO_3 grown by shockwave at energy 120 mJ. It can be seen that at 1 minute, the most probable value for the number of crystals occurs at width 14.1 μm . Figures 4.18 (b) and (c) show that the crystal width has shifted to 36.7 μm and 41.8 μm respectively. While, in figure 4.18 (d) the crystals mean width grow to 63.7 μm .

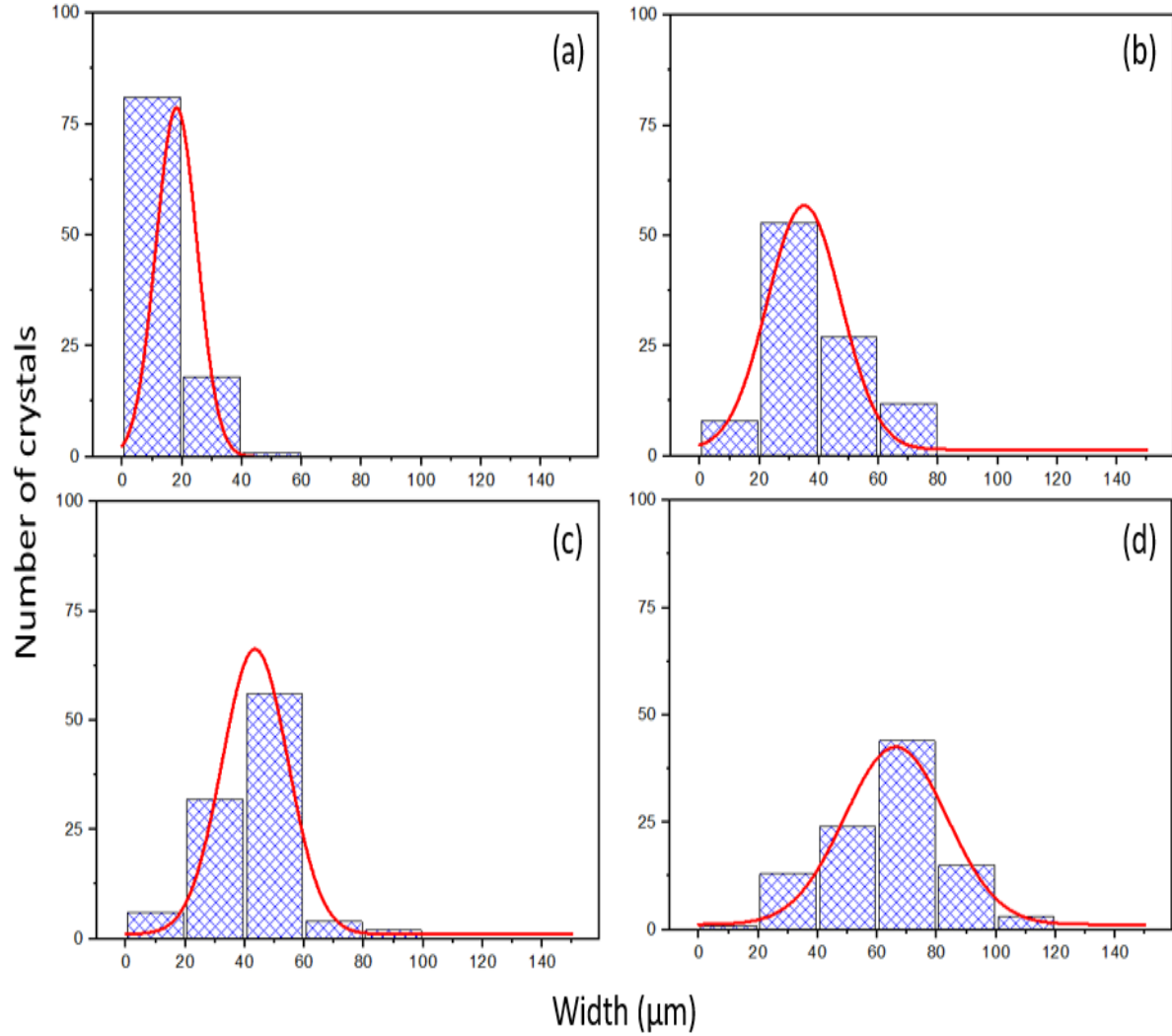


Figure 4.18: Width distributions of KNO_3 crystals grown by non-photochemical technique at energy level 120 mJ at (a) 1 min, (b) 3 min, (c) 5 min, and (d) 7 min.

The length distribution of the generated crystals of KNO_3 formed non-

photochemically at energy 130 mJ is displayed in Figure 4.19. Figure 4.19 (b) and (c) demonstrate that the crystal length had shefted to 140.2 μm and 249.1 μm , respectively, and that at 1 minute, the most likely value for the number of crystals occurs at length 104.5 μm . In contrast, the mean length of the crystals increases to 361.1 μm in figure 4.19 (d) after 7 minutes time elapse.

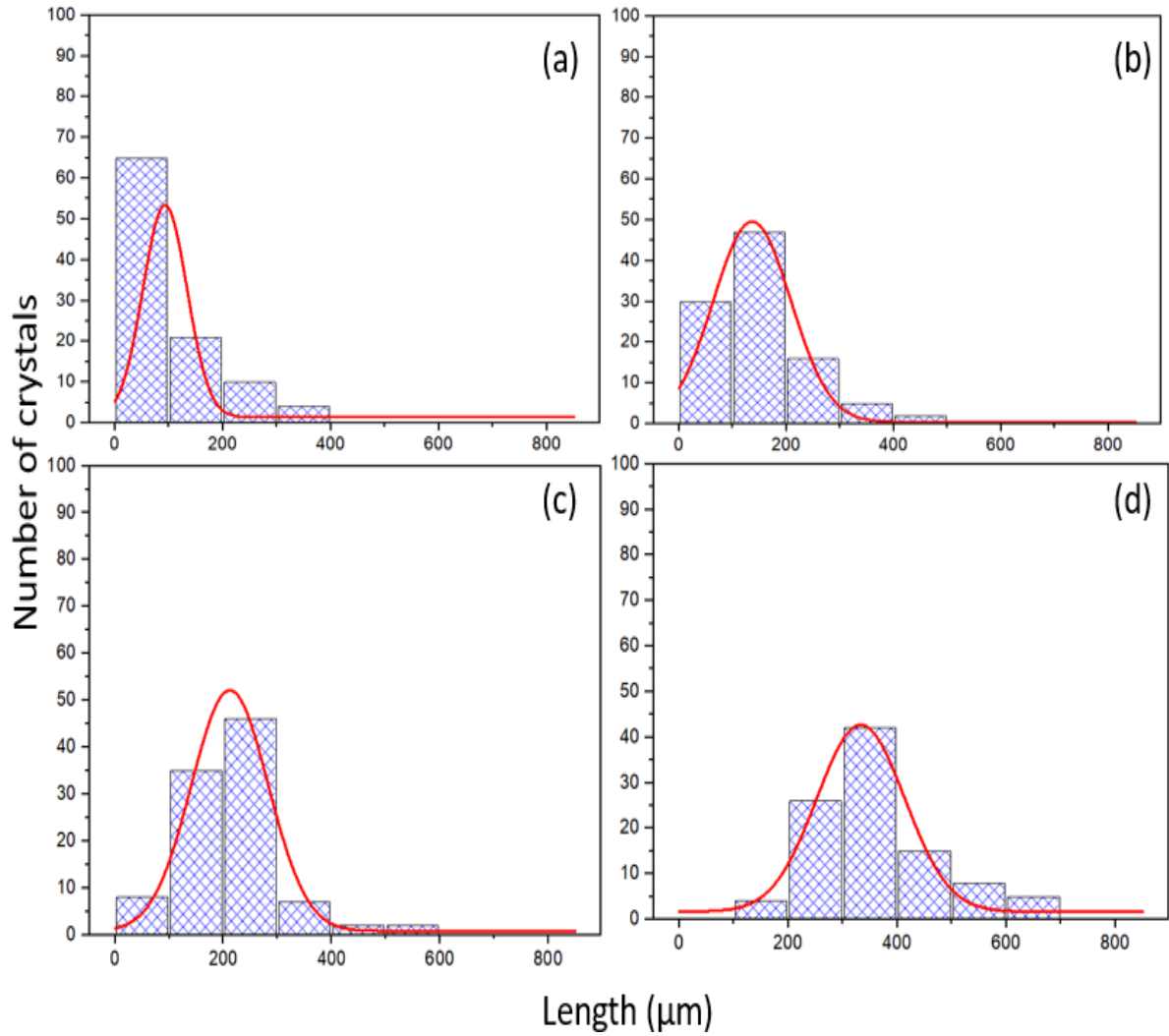


Figure 4.19: Length distributions of KNO_3 crystals grown by non-photochemical technique at energy level 130 mJ at (a) 1 min, (b) 3 min, (c) 5 min, and (d) 7 min.

The width distribution of the generated crystals of KNO_3 formed non-

photochemically at energy 130 mJ is displayed in Figure 4.20. Figure 4.20 (b) and (c) demonstrate that the crystal width had shefted to $46.9 \mu\text{m}$ and $41.8 \mu\text{m}$, respectively, and that at 1 minute, the most likely value for the number of crystals occurs at width $28.3 \mu\text{m}$. In contrast, the mean width of the crystals increases to $63.7 \mu\text{m}$ in figure 4.20 (d).

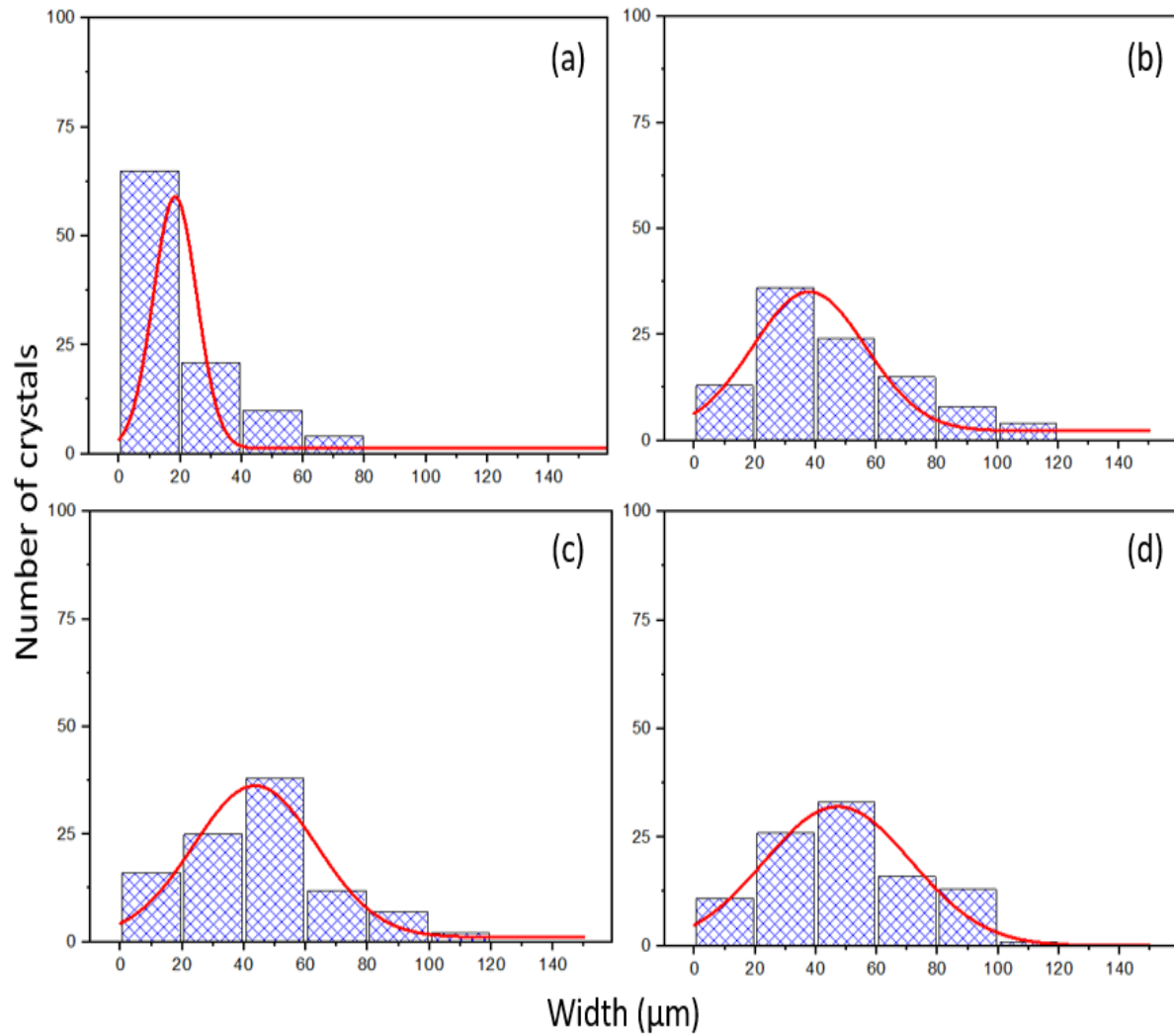


Figure 4.20: Width distributions of KNO_3 crystals grown by non-photochemical technique at energy level 130 mJ at (a) 1 min, (b) 3 min, (c) 5 min, and (d) 7 min.

The length distribution of 100 KNO_3 crystals, which were created non-

photochemically at an energy of 140 mJ, is displayed in Figure 4.21. In Figure 4.21 (b) and (c), the crystal long had shefted to 196.6 μm and 384.1 μm , respectively. The length of 149.6 μm is the most likely value for the number of crystals at one minute elapse. On the other hand, the average crystal length increases to 473.3 μm in figure 4.21 (d) at 7 minutes time elapse.

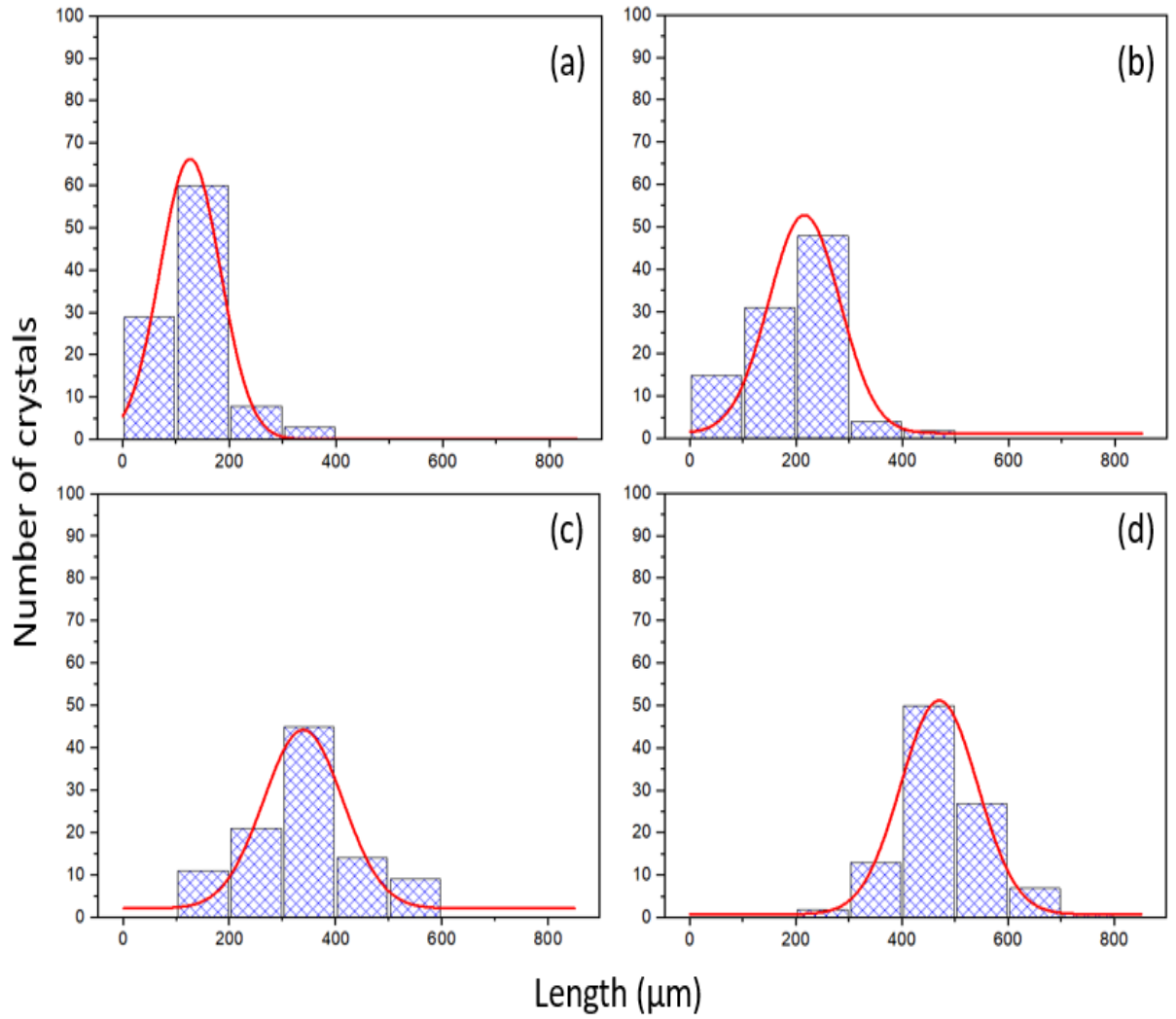


Figure 4.21: Length distributions of KNO_3 crystals grown by non-photochemical technique energy level 140 mJ at (a) 1 min, (b) 3 min, (c) 5 min, and (d) 7 min.

Figure 4.22 shows the width distribution of 100 KNO_3 crystals that were produced

non-photochemically at an energy of 140 mJ. The crystal width had shefted to 52.6 μm and 55.9 μm , respectively, as shown in Figures 4.22 (b) and (c). At 1 minute, the width of 34.5 μm is the most plausible value for the number of crystals. In contrast, in figure 4.22 (d), the average crystal width increases to 58.4 μm .

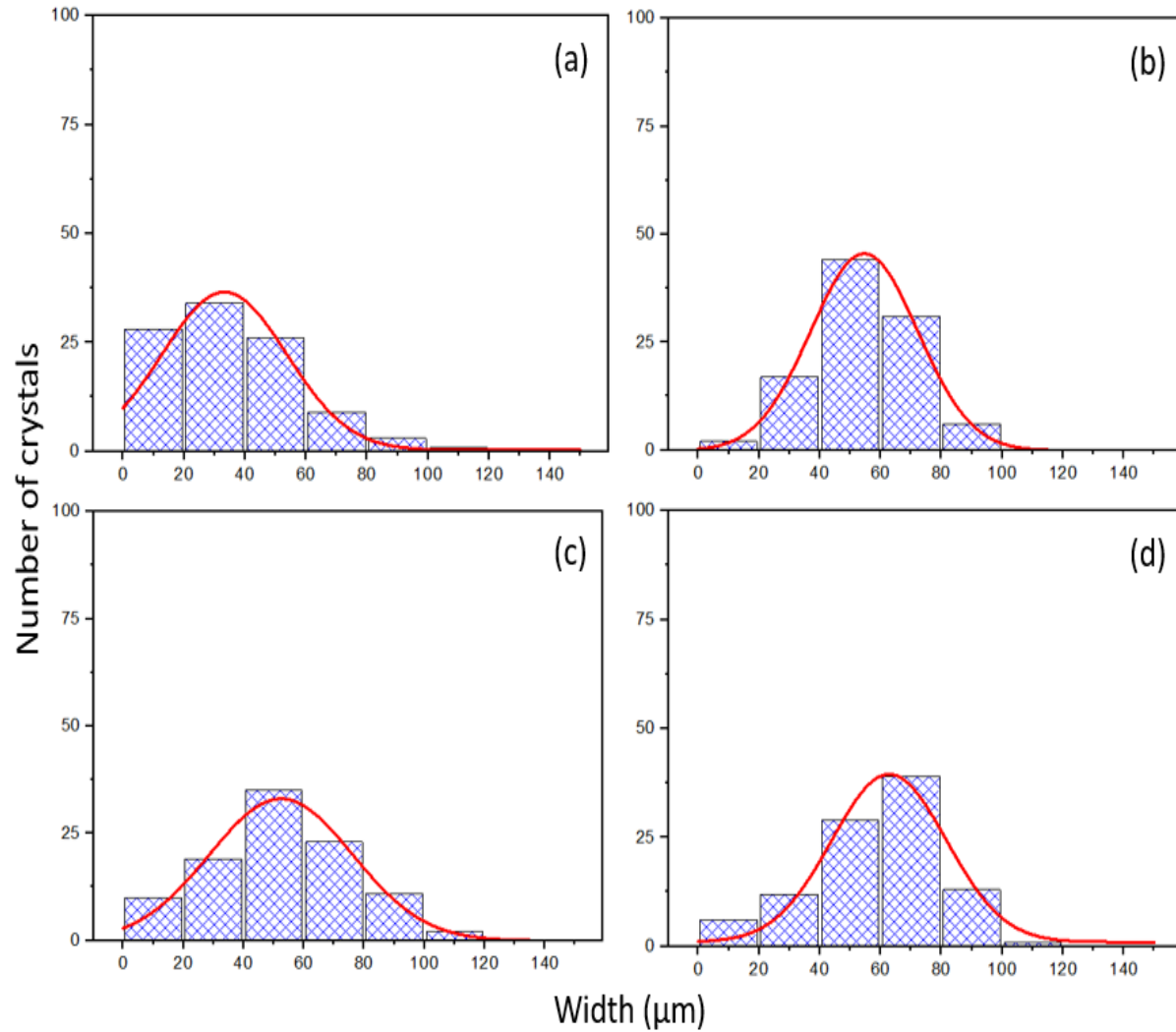


Figure 4.22: Width distributions of KNO_3 crystals grown by non-photochemical technique at energy level 140 mJ at (a) 1 min, (b) 3 min, (c) 5 min, and (d) 7 min.

The length distribution of 100 KNO_3 crystals that were created non-photochemically at an energy of 150 mJ is displayed in Figure 4.23. As can be seen

in Figure 4.23 (b) and (c), the crystal length had increased to $348.8 \mu\text{m}$ and $368.6 \mu\text{m}$, respectively. The length of $175.5 \mu\text{m}$ is the most likely number of crystals at 1 minute. On the other hand, the average crystal length increases to $504.5 \mu\text{m}$ at 7 minutes in figure 4.23 (d).

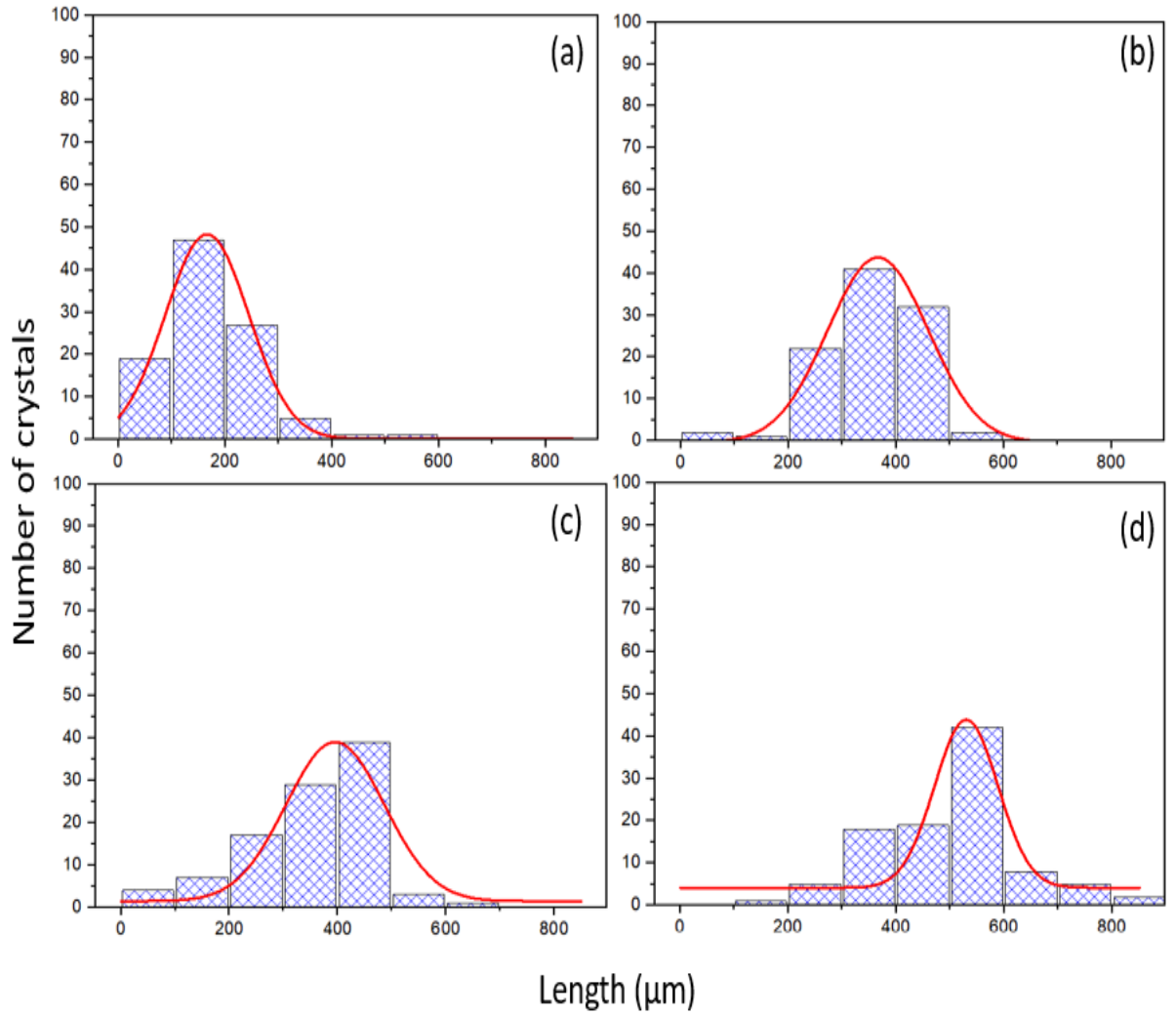


Figure 4.23: Length distributions of KNO_3 crystals grown by non-photochemical technique at energy level 150 mJ at (a) 1 min, (b) 3 min, (c) 5 min, and (d) 7 min.

The width distribution of the 100 KNO_3 crystals generated non-photochemically at an energy of 150 mJ is displayed in Figure 4.24. In Figure 4.24 (b) and (c), the

crystal width had grown to $61.1 \mu\text{m}$ and $64.2 \mu\text{m}$, respectively. The most likely width for the number of crystals at 1 minute is $41.0 \mu\text{m}$. In comparison, the average crystal width rises to $70.3 \mu\text{m}$ at 7 minutes in figure 4.24 (d).

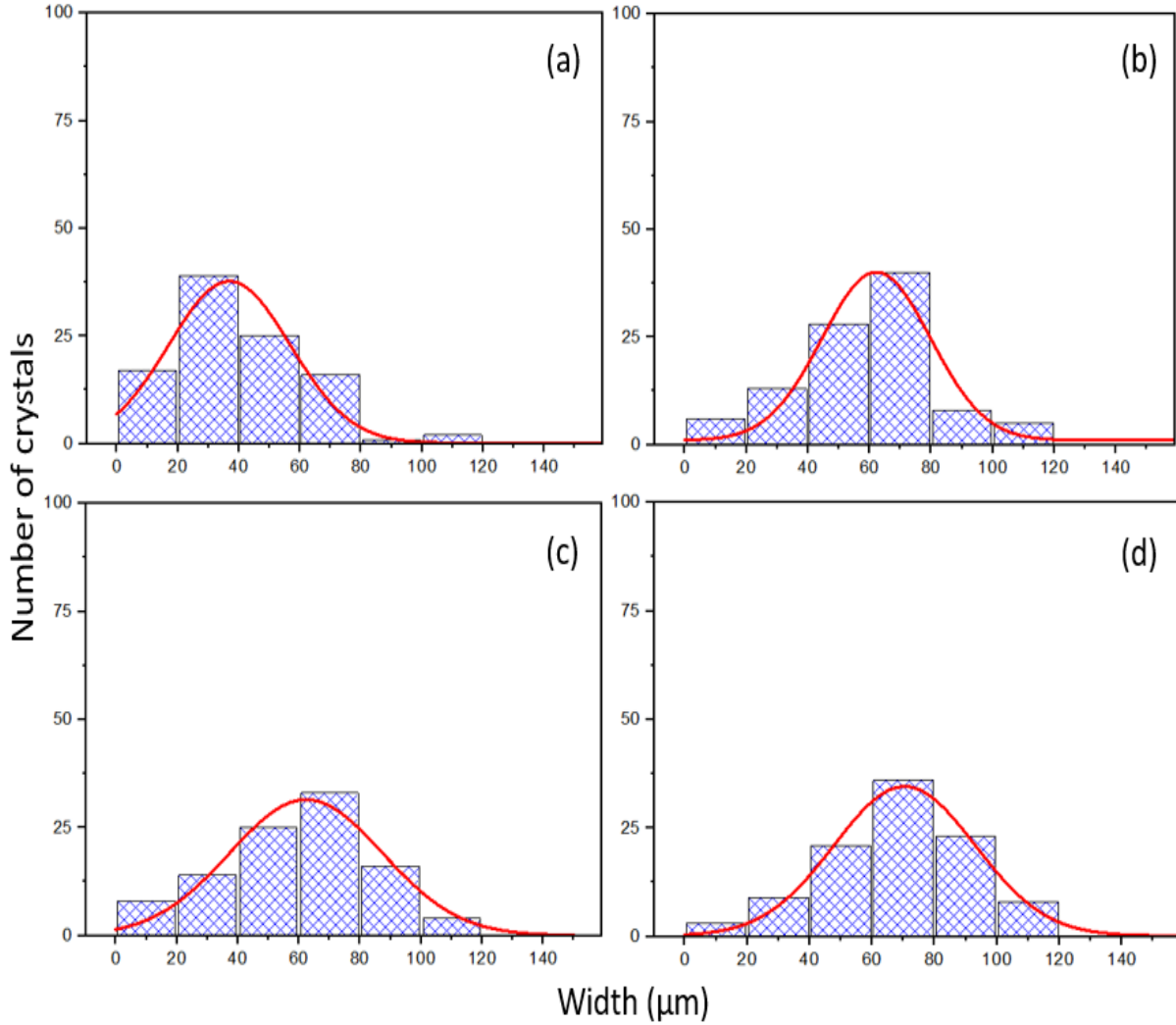


Figure 4.24: Width distributions of KNO_3 crystals grown by non-photochemical technique at energy level 150 mJ at (a) 1 min, (b) 3 min, (c) 5 min, and (d) 7 min.

The length and width size distributions of the obtained KNO_3 crystals generated by direct laser single shots at various energy and growth periods are shown in Figures [4.9, 4.11, 4.13, and 4.15], and Figures [4.10, 4.12, 4.14, and 4.16] respectively. A

Gaussian distribution provided the best fit for the histograms showing the number of crystals as a function of the length and width of the formed crystals. We observed that the distribution of crystals, whether their length or width, were shefed to the right, which indicates crystal growth over time for all measurements, and as the energy increases, the distribution becomes wider. After growing for one minute, the lowest mean length and width of the formed crystals were determined to be $23.9\ \mu\text{m}$ and $10.5\ \mu\text{m}$, respectively. Remarkably, we discovered that the developed crystal's mean length and width both increase with increasing time and energy. Surprisingly, after 7 minutes, the majority of the crystals had fractured or adhered to one another, making it challenging to determine their exact lengths at 140 mJ/pulse and 150 mJ/pulse of the laser's energy, as seen in Figure 4.13 and Figure 4.15. Also, there were not many intact crystals available to measure the crystal's length and width continuously when the energy level was 160 mJ/pulse. There is also another way that energy affects the quantity of crystals that are formed; we find that the quantity of crystals increases as laser energy increases. The size distribution of crystals formed by pure shockwaves was the sharpest, as seen in Figures [4.17-4.24]. Furthermore, the presented data imply that shockwave crystallization tends to create a smaller and sharper size distribution of crystals than direct laser-induced crystallization, as can be seen in Table 4.2. A logical justification arises from the distinct region of influence of these crystallization methods, since the pure shockwaves were predicted to impact a larger volume of solution than that impacted by direct laser-induced crystallization. Because of this, shockwave crystallization has a far higher nucleation site production capacity than laser-induced crystallization. Shockwave-produced nucleation sites gradually vie for

the extra solute in the solution. In comparison to crystals created by direct laser induction, this will result in the generation of numerous smaller crystals [1]. The crystal length and width mean values produced with two alternative methods, direct laser and shockwave, at varied laser energy (120, 130, 140, and 150 mJ/pulse) and time intervals (30 sec, 1, 2, 3, 5, and 7 minutes) are displayed in Table 4.2. The crystal length and width in both techniques typically grow with laser energy and time. For example, using the direct laser technique, the crystal length rises at 120 mJ from 23.9 μm at 1 minute to 367.9 μm at 7 minutes. The shockwave technique shows a similar pattern, with the length increasing from 30.5 μm to 310.1 μm . Furthermore, compared to the direct laser approach, shockwave tends to yield significantly bigger crystal dimensions at shorter time intervals, especially at lower laser energies, as demonstrated at 120 mJ for 1 and 3 minutes. But at higher energies, like 150 mJ, the direct laser technique produces much longer crystals; at 3 minutes, it reaches 737.1 μm , while the shockwave technique only manages 348.8 μm . This indicates that the direct laser approach promotes faster crystal formation than the shockwave technique at higher energy levels.

4.4 Speed of Sound Measurement in KNO_3 Solution

To make the sound waves reflect back to the pulser/receiver probe, the ultrasonic transducer was positioned on one edge of the Plexiglass cylinder designed specifically for this experiment, while the other end was sealed with steel. The transducer is placed

Table 4.2: Display the length and width mean values.

-		Direct Laser		Shockwave	
Laser Energy (mJ)	Time (min)	Mean Length (μm)	Mean Width (μm)	Mean Length (μm)	Mean Width (μm)
120	1	23.9	10.5	30.5	14.1
120	3	82.5	45.4	129.1	36.7
120	5	249.5	67.7	233.3	41.8
120	7	367.9	71.2	310.1	63.7
130	1	98.4	33.9	104.5	28.3
130	3	203.8	50.5	140.2	46.9
130	5	425.0	59.5	249.1	41.8
130	7	493.7	72.6	361.1	63.7
140	0.5	63.7	-	-	-
140	1	191.8	41.4	149.6	34.5
140	2	233.7	-	-	-
140	3	297.5	74.7	196.6	52.6
140	5	-	75.8	384.1	55.9
140	7	-	80.2	473.3	58.4
150	0.5	192.2	-	-	-
150	1	355.8	90.1	175.5	41.0
150	2	404.9	-	-	-
150	3	737.1	102.2	348.8	61.1
150	5	-	104.9	368.6	64.2
150	7	-	110.0	504.5	70.3

with the intention of initiating and then receiving ultrasonic pulses. Measurement of the exact distance (L) between the pulser/receiver prob and the end of the cylinder (13.48 mm) and the time it takes for a pulse to travel and return to the transducer (pulse-echo) (t) are the two methods used to measure the speed of sound, and the speed of sound can be found using the simple equation:

$$v = \frac{2 \times L}{t} \quad (4.1)$$

The experimental apparatus for measuring the speed of sound was first tested to measure the speed of sound of distilled water with an error of measurement of 1.05%, and then it was applied to the crystallization process in nitrate salts. An example of echo pulses reflected by the stainless steel boundary is shown in Figure 4.25.

It was feasible to measure the speed of sound in solutions as a function of saturation level in real time using the ultrasonic transducer in conjunction with the

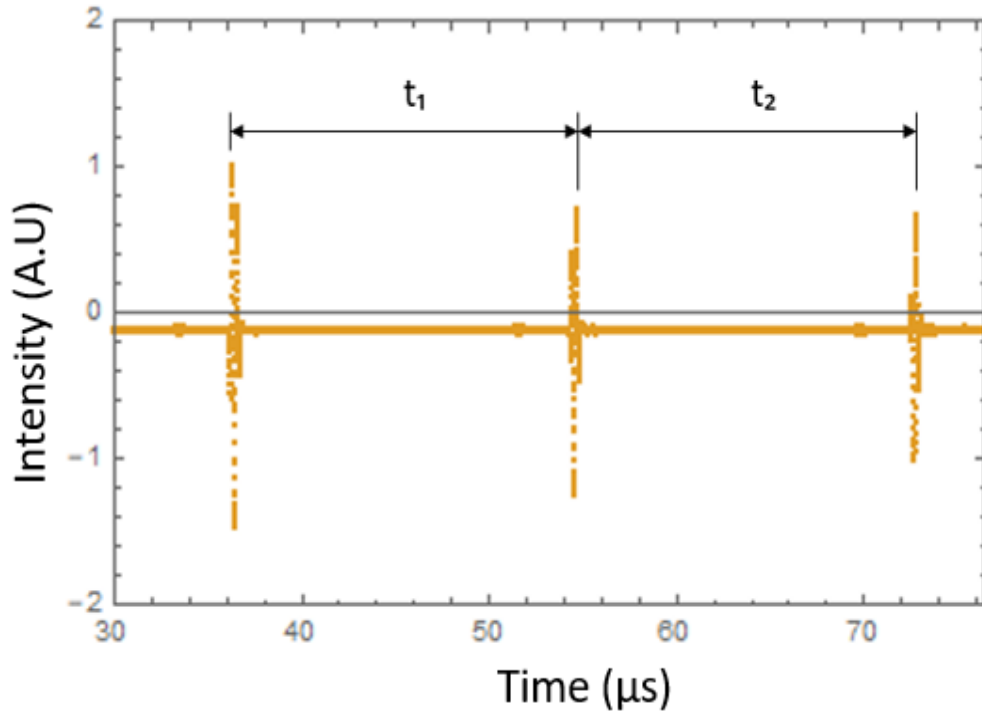


Figure 4.25: Echo pulses received by the transducer in supersaturated aqueous potassium nitrate solution.

pulser/receiver equipment. The potassium nitrate results at various saturation levels are displayed in Table 4.3 along with the speed of sound.

Saturation level (g/ 100 L)	Speed of sound (m/s)	Speed of sound after crystallization (m/s)
0.1	1501.94	1503.63
0.3	1520.59	1523.16
1	1577.53	1581.23
1.3	1601.90	1619.22

Table 4.3: The table displays the speed of sound results in potassium nitrate in different saturation levels.

The speed of sound in a potassium nitrate solution at various saturation levels is depicted in Figure 4.26.

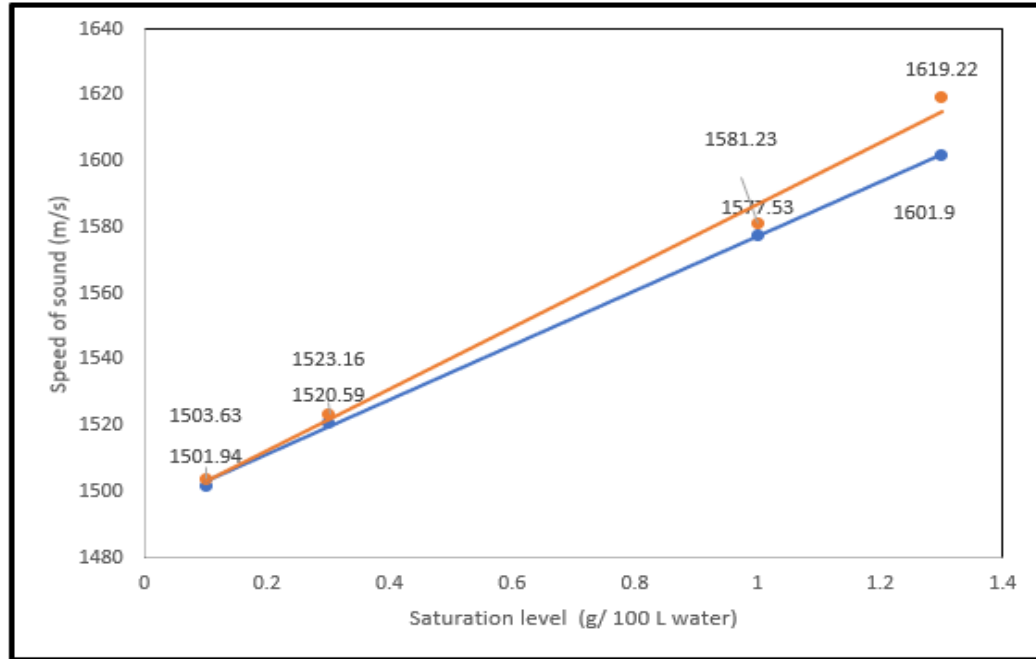


Figure 4.26: The figure shows the speed of sound in potassium nitrate at different saturation levels, both before (blue line) and after (orange line) exposure to the laser.

The sound speed before and after the solution is subjected to a laser is compared. The speed of sound in the potassium nitrate solution rises with increasing saturation level both before and after laser irradiation. At every saturation level, the orange line (following laser exposure) continuously displays a faster sound speed than the blue line (before to laser exposure). This implies that the speed of sound in the solution has risen due to the crystallization induced by laser exposure. One hypothesis is that the laser irradiation might have changed the properties of the solution, such as raising its temperature, or it might have been related to the solution's increased density. The speed of sound increases because sound waves are often transmitted more quickly through dense media.

CHAPTER 5

CONCLUSION

The chemical potential that can be utilized by exposing the solution to laser light is a significant driving force for crystallization. In order to lower the free energy barrier for nucleation, shockwaves have been created in aqueous nitrate salt solutions using a nanosecond pulsed Nd-YAG laser. Compared to crystals produced using traditional procedures, the technology enables us to generate crystals more quickly and with higher quality. While nitrate salt crystals generated by laser-induced shock waves were clearly smaller in size and had a finer size distribution, conventional crystallization without laser irradiation produced irregular and bulky crystals with a wide size distribution. The nucleation rate of cluster formation from solution can be linked to the quality of the crystals.

The length and width of the crystals expand together with the amount of time we leave the solution following exposure to a single laser pulse before harvesting the crystals. Moreover, as the laser energy increased, both the width and length of the crystals grew.

Surprisingly, after 5 minutes, most crystals had either fractured or adhered to one

another, making it difficult to accurately measure their lengths at 140 mJ and 150 mJ of the laser's energy. And there weren't many intact crystals available to measure the crystals' length and width continuously when the energy level was 160 mJ.

The crystallization of nitrate salt was accelerated by the speed of sound. Additionally, by measuring the sound speed at various saturation levels, we discovered that the sound speed increases with both saturation level and laser irradiation. This suggests that even in undersaturated solutions, crystallization will occur, but the size of the crystals will be too small to reach the critical size, meaning they cannot grow into larger crystals.

Laser-induced crystallization creates a novel nucleation control and expands the field of crystallization research beyond what can be achieved with traditional techniques.

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3. Watheq Al-Basheer, Musab Hashim, Ahmed M. El-Zohry, Abdulaziz Aljalal, Khalid Gasmi "Single-shot laser-induced shockwave crystallization in aqueous potassium nitrate solution" (Under preparation to be submitted to ACS Omega).