



Growth And Characterizations Of L-Tartaric Acid Single Grown By Solution Technique

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Abstract

The single crystals of LTA were cultivated through the Slow Evaporation Solution Technique (SEST). Analysis via Powder X-ray Diffractometry (PXRD) authenticated the monoclinic crystal structure, while high-resolution analysis further corroborated these findings, ensuring originality and authenticity. Optical study demonstrated the high optical transparency (85%). Photoluminescence spectroscopy illustrated the pl emission at $\lambda = 388\text{nm}$ and optical band gap 3.2 eV. The SHG efficiency of LTA single crystal (6.61) is comparatively greater than the referenced (KDP) single crystal (6.08). Thermal analysis revealed that the crystal is thermally stable up to 170°C. Etching analysis confirms that the surface of the as grown crystal is having very less defects while the etched crystals surface is having identical rectangular etch pits in shape. The etch pits pattern remains same but the size of etch pits increases with increasing the etching time. Hence, the as-grown LTA single crystals hold promise as a prospective candidate for Nonlinear Optical (NLO) materials, as well as in electronic and optoelectronic devices.

Keywords

"LTA", "Photoluminescence", "PXRD", "Etching Analysis", "Optical Transparency", "Optoelectronic Devices"

1.1 Introduction to Solids

Solid is one of the four fundamental states of matter (the other being liquid, gas and plasma). It is well known fact; most of the materials can possess all three states (solid, liquid and gas) under suitable pressure and temperature [1.1]. In solid state physics, we study the character of those materials which are found in solid state form at room temperature and they are generally divided into three categories on the basis of their crystallinity, crystalline (crystal) solid, semi-crystalline (polycrystalline) solid and non-crystalline (amorphous) solid.

1.1.1 Crystalline Solids

A crystal or crystalline solid is a solid whose constituent particles (atoms, molecules, or ions) are arranged in a three dimensional periodic manner. In other words, it has a reticular structure. The properties of crystalline solid.

- They have characteristic geometrical shape.
- The LTA single crystals exhibit distinct melting and boiling points,
- They are bounded by planes and faces.
- When crystalline solids are rotated about an axis, their appearance does not change, i.e. they are symmetrical.
- Crystalline solids could be cleaved at fixed cleavage planes.
- Physical properties of crystalline solids are different in different directions, i.e. they are anisotropic.

1.1.2 Why the Material should be in the form of a Single Crystal?

The ordered array of atoms in repeated pattern, showing characteristic symmetry elements, by which entire block of the material is built is called single crystal. In single crystal form, solid materials are in most stable state and their properties can be well predicted or estimated in this form. Many useful properties get masked/deteriorated or even completely die out if the material is not in its single crystal form. Therefore, single crystal form is an excellent foundation of modern technology.

Single crystal growth helps us to study many physical properties of solids and effects of grain boundaries. The full range of tensor relationship between applied physical cause and observed effect (property) can be obtained only if the full internal symmetry of the crystal structure is maintained throughout the specimen. The grain boundaries present in the crystal and the part played by imperfections are helpful in determining the physical and chemical properties of solids [1.2].

1.1.3 Importance of Single Crystals in Modern Technology

Growth of single crystals is an essential component of the fundamental research and the grown crystals are the essential requirement of the advance technologies of modern science. Single crystals are required in many important technologies like microelectronics, optoelectronics, communication, computers, photonics, lasers, information science, biosensors and nuclear science etc. In addition to this, they are also required for production of high-efficiency photovoltaic cells for renewable energy, detectors for radiation imaging and fabrication of long-lifetime bright light emitting diodes etc.

Due to the unlimited capacity of data storage, processing and communication, nonlinear optical (NLO) crystals are expected to play a major role in the technology of photonics. Radiation resistant high optical nonlinear crystals are proved to be very important for laser fusion energy due to their ability of generating higher harmonics. The ever-increasing application of semiconductor-based electronics creates an enormous demand for high quality semiconducting, ferroelectric, and piezoelectric and oxide single crystals.

Thus, the large-scale use of crystals in various technologies has made the study of growth of single crystals of different technological materials an interesting and essential field of research. Single crystal technology is now treated to be the mother of almost all the recent technologies of the modern science, which continuously changing the life style of mankind.

1.2 Introduction to Crystals

1.2.1 Symmetry Elements in Crystalline Solids

In an extended array, such as atomic pattern of a crystal, the symmetries involving translation, rotation, reflection, inversion, or their compatible combinations are found to occur. The characteristic feature of these symmetries is that the translation operation repeats an object infinite number of times, while other operation (such as rotation, reflection, inversion, or their combination) repeat it only a finite number of times. Further, the operation like translation or proper rotation leave the “motif” (a fundamental

group of atoms or molecules) unchanged whereas the operations like reflections, inversion or improper rotations change the character of the motif from a right handed to a left one and vice versa. A symmetry element is defined as an imaginary point, line or plane in a body (object) about which an appropriate symmetry operation can be performed to transform it to self coincidence. Linking of this symmetry to a mathematical tool is called **group theory**. This is very valuable in illustrating bonding and spectroscopic properties of molecules.

A three-dimensional periodic pattern, or crystal, can possess various symmetry elements, including rotation axes, mirror planes, inversion centers, and glide planes.

- (i) Pure Translation
- (ii) Proper Rotation
- (iii) Inversion Centre

Pure Translation

A lattice is said to possess translation symmetry if it is periodic along all its crystallographic directions as shown in **Fig. 1.1**. Translational symmetry is an integral part of a lattice. The existence of all other symmetry elements must conform with the translational periodicities. This is defined by the equation:

$$\mathbf{T} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c} \quad (1.1)$$

where, n_1 , n_2 and n_3 are arbitrary integers and a , b , c are primitive translation vectors.

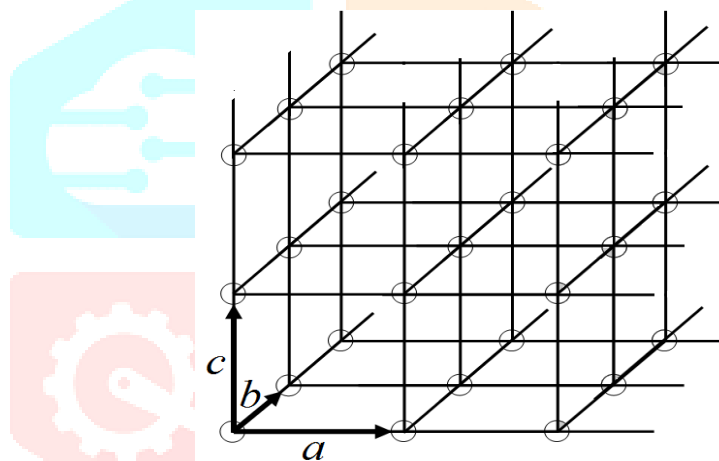


Fig. 1.1 Translation symmetry in crystal

The Proper Rotation

simplest way of representing the operation for the proper rotation is shown in **Fig. 1.2**. One can think of a line or axis passing through the centre and normal to the figure so that the geometrical figures are represented by a rotation through any angle $\phi = 2\pi/n$ about the axis of rotation, the axis is said to have n -fold symmetry. However, because of the reticular structure of the crystals, only 1-, 2-, 3-, 4- and 6-fold

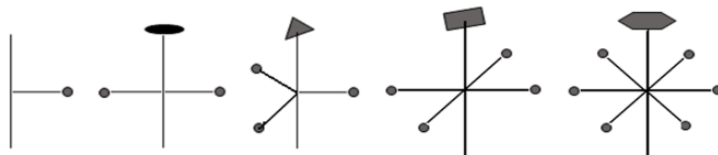


Fig. 1.2 Proper rotations

rotational symmetries are possible. They are known as symmetry elements corresponding to proper rotations, consequently, it means that a crystalline solid can possess neither 5-fold nor any other rotational symmetries higher than 6-folds.

Inversion Centre (Centre of Symmetry)

This is a symmetry operation similar to reflection, with the difference that reflection occurs in a plane of mirror, while inversion is equivalent to reflection through a point called inversion centre or centre of symmetry. In the other words, it is a point such that any line drawn through it will meet the surface of the object/crystal at equal distance on either side as shown in **Fig. 1.3**. Thus the inversion center or the

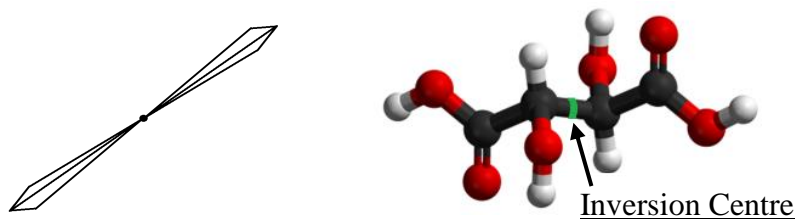


Fig. 1.3 Inversion of an object and LTA molecules

centre of symmetry has the property of inverting all space through a point. It is important to mention here that a crystal may possess a number of planes or axes of symmetry but it can have only one centre of symmetry [1.3]. The molecules of L-tartaric Acid have a center of symmetry and its inversion centre is shown in figure.

1.3 Miller Indices, Planes and Direction

1.3.1 Miller Indices

Miller introduced a system to select a plane in a crystal. To specify a plane and a direction within a crystal, he introduced a set of three numbers, uniquely defining their orientation. This set of three numbers is known as Miller indices of concerned plane or direction. The geometric characteristics of a crystal, represented by lattice points, are termed as rational. Thus a lattice point (site) with respect to another lattice point (site) is a rational point, a row of lattice points is a rational line and a plane defined by the lattice points is a rational plane. All other features are irrational. It is necessary to have appropriate notations to represent their rational features. The notation conventionally employed to describe lattice points, directions, and planes is termed as Miller indices.

1.3.2 Miller Indices of a Plane

A crystal may be considered as an assembly of a number of equidistant parallel planes passing through the lattice points and are called lattice planes. For a given lattice, these sets of planes can be selected in a number of ways. The interplanar spacing of parallel planes is fixed but for different sets of planes the interplanar spacing varies and it also depends on the density of lattice points. The indices of a plane are those integers in parentheses which identify the particular plane and the set of parallel planes is fixed but for different sets of planes the interplanar spacing varies and it also depends on the density of lattice points. The indices of a plane are those integers in parentheses which identify the particular plane and distinguish it from a given from all others. For example, Miller indices of (100), (110) and (111) planes in a cubic crystal are shown in **Fig. 1.4**

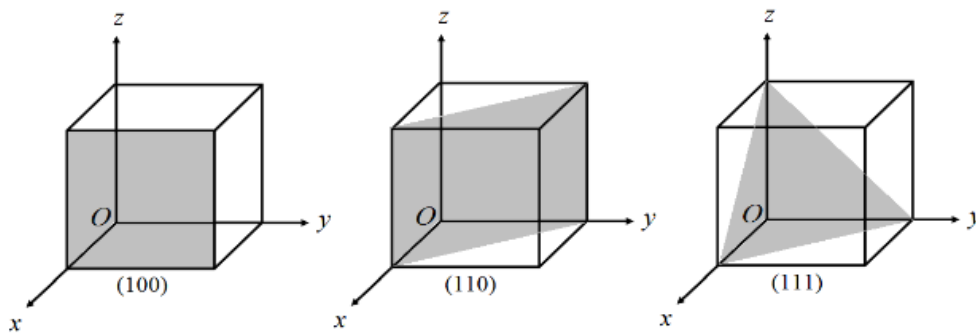


Fig. 1.4 Miller indices of (100), (110) and (111) planes in a cubic crystal

1.4 L-Tartaric Acid

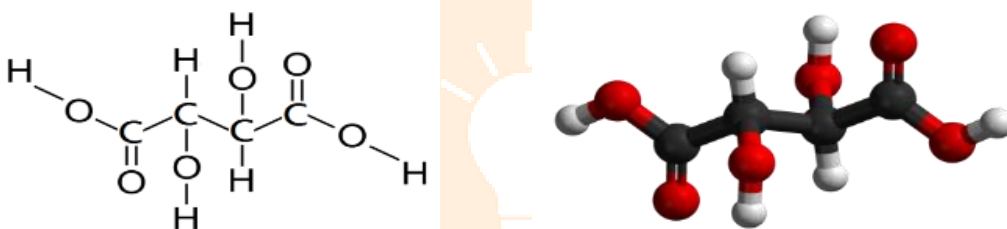


Fig.1.5 Chemical structure of L-Tartaric Acid

Properties

• Chemical formula	$C_4H_6O_6$ (Basic formula)
• Molecular weight	$150.087 \text{ g mol}^{-1}$
• Crystal structure	Monoclinic
• Space group	$P2_1$
• Lattice parameters	$a = 6.20, b = 6.01$ and $c = 7.72$
• Appearance	Colorless
• Density	$1.79 \text{ g/ml (H}_2\text{O)}$
• Mechanical behavior	Strong
• Melting point	$171\text{--}174 \text{ }^\circ\text{C}$
• Solubility in water	$133 \text{ g/100ml (20 }^\circ\text{C)}$

Applications

- This is an efficient nonlinear material which is useful in second harmonic generation (SHG).
- Its SHG efficiency is comparable to that of KDP while the laser damage threshold value is higher than KDP.

2.1 Methods of Crystal Growth and Characterization Techniques Used

The crystals have attracted human civilization from prehistoric times owing to their beauty and rarity. But now their large-scale applications make them the basic pillars of the world of modern technology. Without crystals, there would be no existence of electronic industries, photonics industry and fiber optic communications.

Crystal growth has long been regarded as one of the most captivating fields of research. Although systematic understanding of the subject of the crystal growth began during the last quarter of the 19th century with Gibbs' phase equilibrium concept based on a thermo dynamical treatment. However, the scientific approach to the field of crystal growth started in 1611 A. D, when Kepler correlated crystal morphology and structure, followed by Nicolous Steno, who explained the origin of a variety of external forms. Since then, crystal growth has progressed steadily to reach its current state.

In the past few decades, there has been a growing interest in crystal growth processes, particularly in view of the increasing demand of materials for technological applications. The commercial production of crystals was started by Auguste Verneuil using himself developed Flame Fusion growth method (1902). He is regarded as the father of crystal growth technology as his principles of nucleation control and crystal-diameter control are adopted in later growth methods from the melt, like Bridgman, Czochralski, Stockbarger, etc. [2.1].

High demand of crystals in the field of semiconductors, polarizer's, transducers, infrared detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, nonlinear optics, piezoelectric, acousto-optic, photosensitive materials and crystalline thin films for microelectronics and computer industries compel the researchers/scientists to make progress in different areas of crystal growth. The contents of the crystals and their insides were explored, analyzed and understood by modern scientific equipment such as PXRD, UV-VIS-NIR, HRXRD, FTIR, FT-Raman, DSC, Micro-hardness, etc.

2.2 Methods of Crystal Growth

Now a day, some new methods and some modification in old methods are available in the literatures for growing single crystals for their particular applications. But fundamentally, new methods are based on already existing methods of crystal growth. They are broadly classified into three categories: solution method, melt method, and vapor method. In the research laboratories, the solution growth and the melt growth methods are commonly used. Here our discussion is confined to the methods only under the solution growth and the melt growth methods and these are following [2.2].

Solution Growth

- (I) Aqueous Solution Method
- (II) Flux Method
- (III) Hydrothermal Method

Melt Growth

- (I) Bridgeman- Stockbargar Method
- (II) Czochralski (CZ) Method
- (III) Zone Refining Method
- (IV) Float Zone Method

Before the use of any method of crystal growth, it is necessary to check the general criteria for assessing a method, which are:

- The universality, i.e., the number of materials to which the technique may be applied.
- The size and quality of the grown crystals are crucial factors in crystal growth research.
- The requirement of chemicals and apparatus.
- The requirement of experience and time.
- Industrial application and cost of per acceptable crystal.

Solution and melt growth in general satisfy all the above said criteria.

2.2.1 Solution Growth

This method is based on the homogeneous solution of two or more substances. In such a solution, a solute substance is dissolved in another substance, known as a solvent. It is very important to mention here that not every solvent is able to dissolve every type of solute i.e., dissolution of a solute in a solvent, in general, depends on the nature/chemical bond of both. Solutions (the homogeneous mixture of solute and solvent) in which the solvent is water are called aqueous solutions.

Slow Evaporation Method

In this method, solute is dissolved in double distilled water at room temperature (~300 K) with continuous stirring for 2-3 days in order to make the highly homogeneous, saturated and transparent solution. To check the homogeneity of solution, it is heated to a few degrees above the saturation temperature. Stirring of the solution is done to overcome the concentration gradient in the crystallizer. Then saturated solution is filtered with a good quality filter paper in a well cleaned beaker. The beaker is covered with a paper having some tiny holes in it to facilitate slow evaporation. Then solution is housed in a dust and vibration free place at same temperature for constant evaporation. If the solvent is non-toxic then the evaporation is allowed in the open atmosphere. After a few days, crystal growth will start. The position of beaker should not be disturbed till the growth is complete. This is to avoid multi nucleation and growth of crystal on the walls of the beaker as they hinder the growth of a good crystal. As the crystals grow to a desired size, they are taken out so that the adjacent crystals do not touch each other and lead to grow with boundaries. In this method, as size of the crystal increases more impurities are found on their faces. Consequently, this method is not suitable to grow bigger size crystals. Although there are some disadvantages but this is the most simple and convenient method for growing small size crystals.

Advantages

- Simple growth apparatus.
- In evaporation method, crystal growth occurs at high temperature. This avoids the formation of any compound which is possible at lower temperature.
- Crystals with minimal variation in solubility with temperature can be cultivated.
- If carried to completion, nearly 100% yield of the solute phase is obtained.

Disadvantages

- Nucleation at the melt surface may be excessive and thus inter-grown crystals may result.
- There is less control over the growth process than in slow cooling, which typically produces better quality crystals.
- The interstitial incorporation of solvent ions into the crystal lattice causes the formation of cloudiness.
- Rate of growth is slow. This can be improved only to a certain extent.

2.3 Characterization Techniques Used

The grown crystals have been studied using the following characterization techniques:

- 2.3.1 Powder X-Ray Diffractometry (PXRD)
- 2.3.2 UV-VIS-NIR Spectroscopy
- 2.3.3 Photoluminescence (PL) Spectroscopy
- 2.3.4 Thermal Analysis
- 2.3.5 Etching Study

2.3.1 Powder X-Ray Diffractometry (PXRD)

According to Bragg's law, when a monochromatic X-rays beam of wavelength λ ($\sim 1.54\text{\AA}$) impinges upon the crystal lattice, each atom acts as a source of scattering

of same wavelength. The crystal acts as a series of parallel reflection planes. The intensity of the reflected

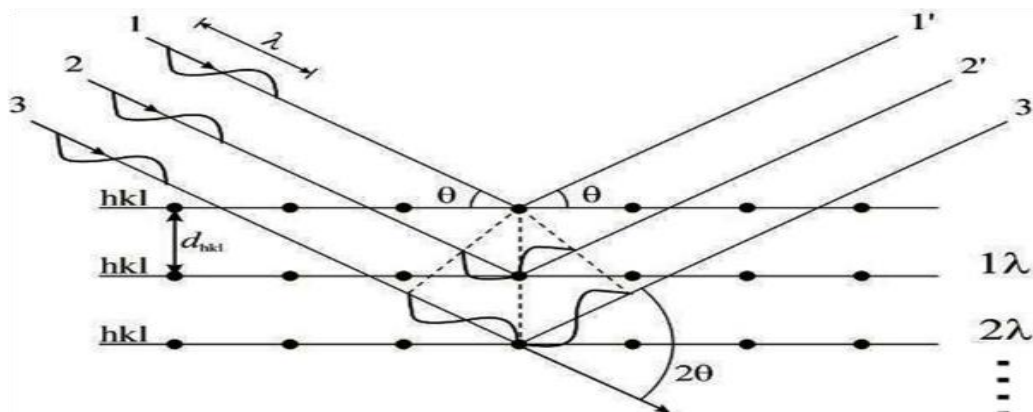


Fig. 2.4: Schematic diagram of Bragg diffraction

beam at specific angles reaches a maximum when the path difference between two reflected waves from two distinct planes equals an integral multiple of the wavelength (λ). The atomic planes are considered to be semi transparent, that is, they allow a part of the X-ray to pass through and reflect the other part, the incident angle θ (The condition for maximum reflection, known as the Bragg angle, occurs when the angle of reflection equals the Bragg angle. In Fig. 2.4, there exists a path difference between rays reflected from plane 1 and the neighboring plane 2 within the crystal. These two reflected rays reinforce each other when this path difference equals an integral multiple of the wavelength. If d represents the interplanar spacing, the path difference is twice the distance $d \sin \theta$, as illustrated in the figure. Therefore, the Bragg condition for reflection can be expressed as:

$$[2d \sin \theta = n \lambda] \dots\dots\dots(2.1)$$

Here, (n) is an integer (order of diffraction) and (d) is the interplanar spacing.

X-ray diffraction study is used to characterize the grown single crystals by preparing the powder to confirm the crystal structure and their lattice parameters. The powder specimen of the crystal can be imagined to be a collection of random oriented tiny crystals, presenting all values of glancing angle to the incident beam. For a given wavelength and a given value of d , there can be only one value of θ which satisfies the Eq. (2.1)

An Introduction to Powder X-ray Diffractometer

A Panalytical PW-1830 based powder X-ray diffractometer shown in Fig. 2.5 (a) was used to characterize the titled compound. The schematic diagram of this is shown in Fig. 2.5 (b). Panalytical PW-1830 is a state-of-the-art, high-quality powder X-ray diffractometer system that is easy to use, highly accurate, and versatile to meet all needs in X-ray diffraction. The heart of the Panalytical PW-1830 diffractometer is the high-precision, two-circle goniometer with independent stepper motors and optical encoders for the theta and 2θ circles. The goniometer, its accessories, and the detector are controlled by an integrated microprocessor. The alignment of the diffractometer is completely computer controlled. It has vertical goniometer. Ni-filter is used to reduce the background white radiation and allow the $\text{CuK}\alpha$ radiation. Proportional counter is used to measure the diffracted intensity. The diffracted beam is monochromatised with focusing graphite monochromator (Bragg- Brentano geometry). The diffractometer is equipped with

a Kratkysmall angle X-ray scattering camera from Anton Paar, with step-scanning motor and scintillator

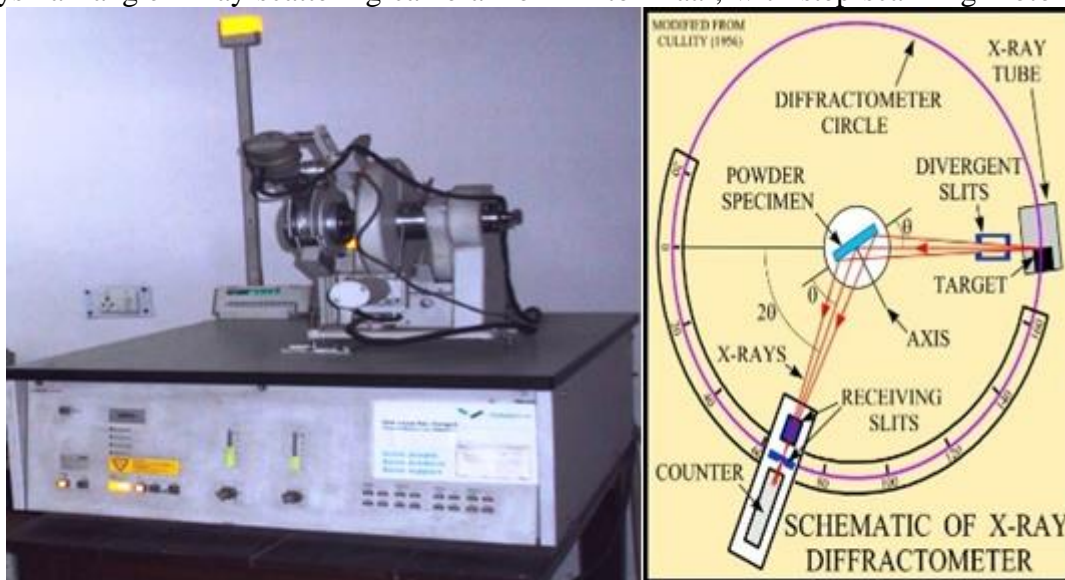


Fig. 2.5: (a) Panalytical PW 1830 Powder X-ray Diffractometer and (b) Schematic view of Powder X-ray diffractometer

counter.

The powder sample should be homogeneous, with a grain size less than 25 microns. When a sample is exposed to a parallel beam of monochromatic X-rays. The atomic lattice of the sample acts as a three dimensional diffraction grating causing the X-ray beam to be diffracted to specific angles. When the sample rotates by an angle θ , the detector automatically rotates by an angle of 2θ to record the intensity of the diffracted beam obtained by the planes Meeting the Bragg's condition at the Bragg angle, denoted as θ , ensures optimal reflection. Full diffractogram can be obtained by recording the diffracted intensity from a start angle (2θ) (~5 degrees in the present case) to the end angle (2θ) (~70 degrees in the present case) with a minimum possible step size (2θ) which is 0.020 degree for this diffractometer. The diffraction pattern is a plot of position (θ) versus intensity (I) of the diffracted beam and provides several informations about the sample. Some of them are given below:

- Angles are used to calculate the inter-planar atomic spacing (d-spacing).
- The (d) values in terms of (hkl) and the peak intensity (I) together are used to identify the material by comparing them with JCPDS data.
- The position (d) of diffracted peaks also provides information about how the atoms are arranged within the crystalline material (unit cell size or lattice parameter).
- Width of the diffracted peaks is used to determine crystallite size and strain in the sample.

To determine the lattice constants and the unit cell volume, the obtained XRD data was compared with ASTM data and also refined with the help of “XPRT High Score Plus” and “POWDERX” software.

2.3.2 UV-VIS-NIR Spectroscopy

Ultraviolet absorption spectra are attributed to a process in which the outer electrons of atoms or molecules absorb radiant energy and undergo transitions to high energy levels. When these electronic transitions are quantized, they are found to depend on the electronic structure of the absorber. Analyzing the absorption of ultraviolet and visible radiation offers a convenient method for studying various inorganic and organic species. It should be noted that the total energy of a molecule is the sum of its electronic energy, its vibrational energy and its rotational energy. It has been observed that the electronic transitions require more energy in comparison to vibrational changes and the latter require more energy than rotational changes inside the molecule. The wavelength range of these techniques conventionally reaches from the UV (190 nm) to the near infrared at 1100 nm.

Theory

When a beam of light with intensity “ I_0 ” passes through an absorbing medium the intensity of emerging beam “ I ” drops exponentially.

This relationship when expressed as Lambert's Law is:

$$I = I_0 e^{-\epsilon c x} \quad (2.3)$$

Where,

I_0 = intensity of incident radiation

ϵ = extinction coefficient ($M^{-1}cm^{-1}$)

c = the molar concentration of the absorber in units of mol/L.

x = path length (cm)

The relation between absorption or absorbance (A) and transmittance for a particular wavelength “ λ ” is given by:

$$T = \frac{1}{10^A} \quad \text{or} \quad A = -\log(T) \dots \dots \dots (2.4)$$

Where, T denotes transmittance, defined as the ratio of the intensity of transmitted light to the intensity of incident light.

$$T = \frac{I}{I_0} \dots \dots \dots (2.5)$$

Using the above equations (2.3), (2.4) and (2.5) we get

$$A = -\log(I/I_0) = \epsilon c x \dots \dots \dots (2.6)$$

Thus according to Beer-Lambert Law (Beer’s Law), the amount of light absorbed by a sample is dependent on its molar extinction coefficient (it is also called molar absorptivity), Path length in cm and molar concentration of the absorber.

$$A = \epsilon c x \dots \dots \dots (2.7)$$

Applications

- It is used for the quantitative analysis and the analysis of mixture.
- Measuring how the concentration of a substance involved in a reaction changes over time.
- The quantification of the variation in concentration of a reactant or product over time.

2.3.3 Photoluminescence (PL) Spectroscopy

Photoluminescence (PL) spectroscopy is a very sensitive technique to characterize the defect states inside the band gap of material [2.3]. PL is the emission of light caused by the irradiation of a substance with other light. The term PL embraces both fluorescence and phosphorescence. They differ in the time after irradiation over which the luminescence occurs. Photoluminescence is commonly utilized in semiconductor devices. (e.g. semiconductor lasers or amplifiers, solar cells, or saturable absorbers). Here, photoluminescence is excited by illumination of the device with light which has photon energy above the band gap energy. The photoluminescence then occurs for wavelengths around the band gap wavelength. The spectrum of the photoluminescence (PL) spectrum and also the dependence of its intensity on the irradiation intensity and device temperature can deliver important information for device characterization. In particular, PL spectra and their intensity dependencies can allow one to determine/investigate:

- (1) The band gap energy and/or the wavelength of maximum gain.
- (2) The composition of ternary or quaternary layers.
- (3) The impurity levels.
- (4) The recombination mechanisms.

Photoluminescence (PL) mappers can spatially resolve the photoluminescence obtained from epitaxially grown wafers and single crystals. For example, PL mappers can reveal a radial dependency of layer thickness or material composition.

2.3.4 Thermal Analysis

A group of techniques in which physical property of a substance and its reaction products is measured as a function of temperature whilst the substance is subjected to a controlled temperature program [2.4]. The flow of heat into a substance can trigger various physical and chemical transformations, aiding in the identification and characterization of a sample. We have employed three methods which are commonly used. These are distinguished from one another by the measured property.

- Differential Scanning Calorimetry (DSC): heat difference
- Thermo gravimetric Analysis (TGA): mass difference
- Differential Thermal Analysis (DTA): temperature difference

Differential Scanning Calorimetry (DSC)

DSC measures the temperature and heat flow associated with transitions in materials as a function of temperature and time. Such measurements provide us quantitative and qualitative information about physical and chemical changes that include endothermic/exothermic processes or changes in heat capacity. To measure DSC, difference in the amount of heat required to increase the temperature is measured as a function of temperature of a sample and a standard reference. During the experiment, both the sample and the reference are kept at nearly the same temperature. Typically, the temperature program for a Differential Scanning Calorimetry (DSC) analysis is arranged in such a way that the temperature of the sample holder increases linearly over time. It's essential for the reference sample to exhibit a clearly defined heat capacity across the temperature range being scanned.

Thermo-gravimetric Analysis (TGA)

TGA is a technique in which changes in sample mass (mass loss/gain) is determined as a function of increasing temperature while keeping constant heating rate, or as a function of time while keeping temperature constant in an atmosphere of nitrogen. TGA (Thermo gravimetric Analysis) can offer insights into various physical phenomena, including second-order phase transitions such as vaporization, sublimation, absorption, adsorption, and desorption. Likewise, TGA can provide information about chemical phenomena including chemisorptions, desolation (especially dehydration), decomposition, and solid-gas reactions (e.g., oxidation or reduction).

Differential Thermal Analysis (DTA)

DTA is a qualitative technique in which the temperature difference between a substance and a reference material is measured as a function of controlled temperature. In Differential Thermal Analysis (DTA), both the material under examination and an inert reference undergo identical thermal cycles, while any temperature variance between the sample and reference is recorded. This temperature difference, known as the differential temperature, is then plotted against time or temperature, yielding a DTA curve or thermogram. Changes in the sample, whether exothermic or endothermic, can be identified in relation to the inert reference. Consequently, a DTA curve provides insights into various transformations such as glass transitions, crystallization, melting, and sublimation. The area under a DTA peak represents the enthalpy change and remains unaffected by the sample's heat capacity.

2.3.5 Etching Study

It is well known fact that the defects in the crystals may destroy the mechanical, optical and electrical properties, which affect the utility of the crystals for device applications. The nonlinear optical properties, laser damage threshold etc., depends on the purity and perfection of the crystals. The etching studies reveal the structural perfection and growth features of the grown single crystals [2.5]. It is an important tool to classify of crystal defects, which is able to develop some of the features such as growth hillocks, etch spirals, rectangular etch pits etc. on the crystal surface. The pattern of etch pits depend on the etchant, etching time and crystal faces. Etch pits are associated with dislocation and dislocation bundles and hence bring out the crystal quality [2.6] For carrying the etching study on the grown single crystals, a mixture of water and acetone was used as an etchant and after that the surface of the crystal was wiped with tissue paper and then its surface was analyzed with the help of optical microscope in the reflection.

3.1 Growth and Characterizations of L-Tartaric Acid Single Grown by Slow Evaporation Solution Technique

In this present chapter, an introduction of L-Tartaric Acid (LTA) having NLO properties and its growth as a single crystal has been discussed in detail. Essential characterizations of LTA have been put forth to check its suitability for NLO application. The materials having NLO properties have been showing the potential applications in the area of laser technology, fiber optic communications and data storage technology etc[3.1]. From this point of view, an optical material should possess large charge transfer and optical transparency with less dislocation density. The single crystals having defects like structural grain boundary or not in the single domain deteriorate the corresponding anisotropic physical, optical and electrical properties [3.2, 3.3]. Therefore, it is very important to grow defect free single crystals in bulk as

they are used for potential applications in different areas of research such as high-density optical data storage, high-resolution printing and spectroscopy [3.4]. Organic nonlinear optical (NLO) materials are currently receiving significant attention due to their notable features such as large optical susceptibilities, inherent ultra-fast response times, and high optical thresholds for laser power in comparison to inorganic materials. A key advantage of organic materials lies in their ability to modify chemical structures, offering a wide range of physical structural diversity and properties to achieve desired NLO characteristics. An example of such a material is L-tartaric acid (LTA), which exhibits a monoclinic crystal system with space group P21. Its SHG efficiency is comparable to that of KDP whereas, the laser damage threshold value is higher than that of KDP [3.8]. The higher solubility of L-tartaric acid (LTA) in water allows for the growth of larger crystals at a lower cost compared to other amino acid nonlinear optical (NLO) [3.6-3.7] materials. Numerous complexes of tartaric acid have been identified for their NLO properties [3.9-3.10]. In this work, we are reporting the good quality bulk single crystals of LTA grown by slow evaporation technique at room temperature. Even though many reports are available on the title compound, but very few reports are available on the structural and optical properties of LTA. So, we have carried out the optical studies by PL, structural by chemical etching, thermal analyses by adopting Differential Scanning Calorimetry (DSC) and electrical conductivity for the first time and analyzed the results. To know its mechanical behavior, hardness study has also been discussed in detail on the basis of different mechanical parameters.

3.2 Experimental

3.2.1 Crystal Growth

The purity of a material is crucial for enhancing its properties. In order to achieve this objective the commercially purchased LTA (~98% purity) was purified by repeated re-crystallization processes and the highly purified material was used to grow the single crystals of LTA. A saturated solution of L-tartaric acid (LTA) was prepared at room temperature by vigorously stirring a mixture of double-distilled water and LTA for approximately 24 hours, following the solubility curve.[3.9]. As-prepared Solution was then filtered in Borosil glass beaker and covered with the perforated plastic sheet. The solution contained beaker was then housed (in constant temperature bath) at same temperature. High-quality single crystals of LTA, exhibiting well-defined facets, transparency, and excellent morphology, were obtained through harvesting. (Fig. 3.1) from the mother solution after a time span of 15 days.

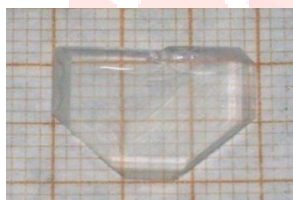


Fig. 3.1: As-grown LTA single crystals

3.2.2 Characterization Techniques

To know the purity and crystal structure of the as grown single crystal, the powder form of the

LTA crystals was scanned in the Bragg diffraction angle range 5–70°, at the rate of 0.02°/s by powder X-ray diffractometer (PW-1830) using nickel filtered $\text{CuK}\alpha$ ($\lambda=1.54056 \text{ \AA}$), supplied by PANalytical. Its crystalline perfection and topography analyses were carried out by adopting double crystal X-ray diffractometer with 12 kW Rigaku rotating anode X-ray generator. The optical transparency was checked by using Perkin Elmer lambda 35, UV-VIS-NIR spectrophotometer in the wavelength region 200–1100 nm. Photoluminescence (PL) spectrum of the sample was recorded by Varian spectrometer using 2.5 kV fluorescence lamp. Differential Scanning Calorimetry (DSC) was performed for the LTA crystals using a Perkin Elmer Pyris 6 DSC in the temperature range from 25 to 400°C with a heating rate of 5°C/min in nitrogen atmosphere. Etching studies of the as-grown single crystal was carried out using the mixture of water and acetone as an etchant.

3.3 Results and Discussions

3.3.1 Powder X-ray Diffraction Analysis (PXRD)

Fig. 3.2 shows the recorded PXRD pattern of the powder of the as-grown LTA single crystal. The general aspect of this PXRD patterns, in particular, the presence of strong and sharp peaks and the absence of diffraction halo, indicate the presence of crystalline phase only. Additionally, they demonstrate the lack of either amorphous or crystalline-amorphous phases. Phase formation [3.11]. The Bragg's reflections were indexed for LTA single crystal and PXRD data was refined by 'CHEKCELL' software. The calculated values of lattice parameters of LTA (**Table 3.1**) are in good agreement with the reported values [3.12], thus confirming the monoclinic crystal system of the as-grown single crystal. The values of lattice constants, calculated using the software expert high score plus are, $a = 7.6983 \text{ \AA}$, $b = 6.0270 \text{ \AA}$ & $c = 6.1959 \text{ \AA}$ whereas, the reported [3.12] values of lattice constants are, $a = 7.722 \text{ \AA}$, $b = 6.005 \text{ \AA}$ & $c = 6.221 \text{ \AA}$. The calculated and reported lattice constants demonstrate a clear agreement, indicating that the growth of LTA single crystals using commercially purchased LTA, recrystallized and employing the solution growth method, impacts the morphology to some degree but does not significantly alter it. the crystal structure [3.13]. The diffraction pattern's Bragg reflections (**Fig. 3.2**) were indexed by comparing the reported JCPDS data file no 72-3533. Analysis of the diffraction pattern reveals that the most intense and sharply defined peak corresponds to the (011) plane, indicating the preferred orientation of the

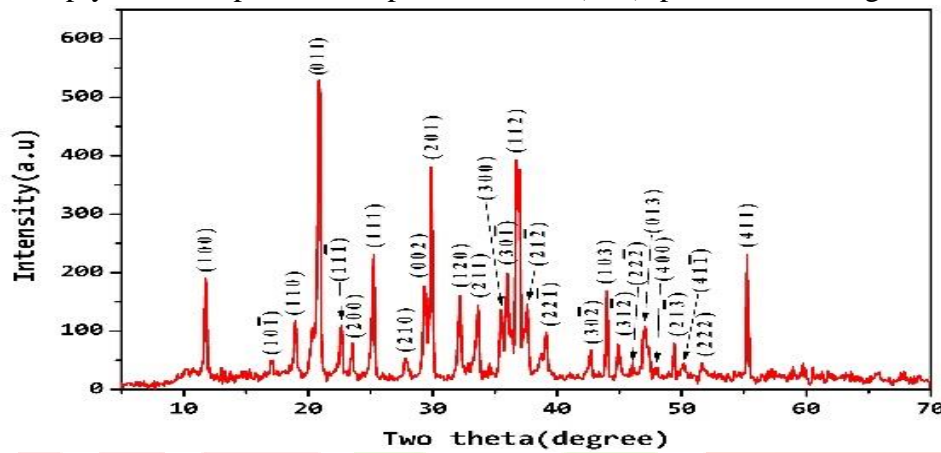


Fig. 3.2: PXRD pattern of the as-grown LTA single crystal

crystallites along [011] direction.

Table 3.1: X-ray powder diffraction data for LTA

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> (Å)	<i>2 Theta</i>
1	0	0	7.59911	11.636
1	0	-1	5.22966	16.940
1	1	0	4.71391	18.810
0	1	1	4.28218	20.726
1	1	-1	3.94517	22.519
2	0	0	3.79955	23.394
1	1	1	3.54768	25.081
2	1	0	3.21157	27.756
0	0	2	3.05146	29.243
2	0	1	2.99717	29.785
1	2	0	2.79444	32.002
2	1	1	2.68215	33.380
3	0	0	2.53304	35.408
3	0	-1	2.50081	35.880
1	1	2	2.44265	36.764
2	1	-2	2.39772	37.479
2	2	-1	2.28423	39.416
3	0	-2	2.14355	42.121
1	0	3	2.05781	43.966
3	1	-2	2.01898	44.857
2	2	-2	1.97258	45.972
0	1	3	1.92691	47.126
4	0	0	1.89978	47.841
2	1	-3	1.84748	49.284
4	1	-1	1.82210	50.017
2	2	2	1.77384	51.476
4	1	1	1.66202	55.223

3.3.2 UV-VIS-NIR Spectral Analysis

The transmittance plays an important role to identify the potential of NLO materials because a given NLO material can be used only if it has a wide transparency range without any absorption at the fundamental and second harmonic wavelengths [3.14.–3.15]. The UV-VIS-NIR transmittance spectrum of the as-grown LTA single crystal of ~2 mm thickness was recorded in the wavelength range of 200 to 1100 nm and is shown in Fig. 4.5. It is clear from the figure that the optical transparency of the crystal is more than 85% for the entire UV-VIS-NIR region. This may be due to the maximum crystalline perfection or defect free LTA single crystals. There is no notable change in the lower cut off wavelength with reported value [3.9]. The absence of absorption of light in the visible region is an intrinsic property of all the amino acids [3.16]. For this reason, this specimen may be used for the conversion of SHG in most efficient way.

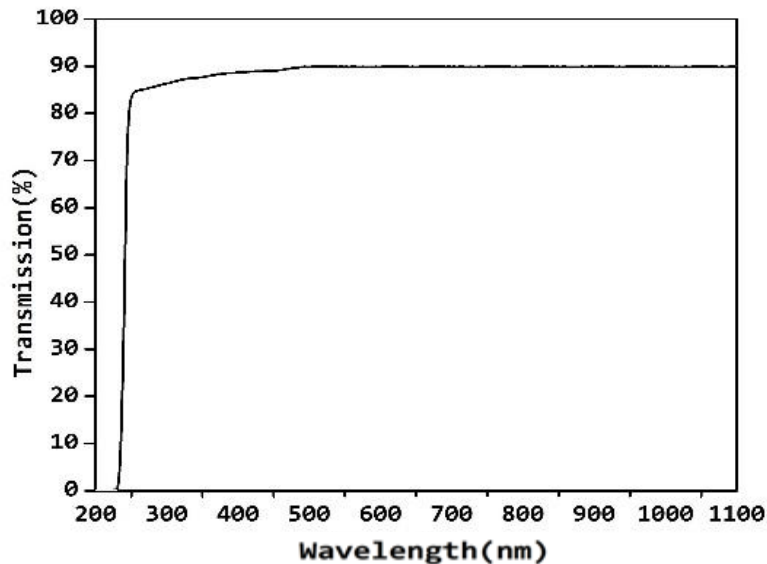


Fig. 3.3 UV-VIS-NIR spectrum of the as-grown LTA single crystal

3.3.3 Photoluminescence Analysis

Photoluminescence (PL) spectroscopy is a very sensitive technique to characterize the defect states inside the band gap of material [3.16]. The photoluminescence (PL) spectrum of the LTA single crystal is depicted in Fig. 3.4. The sample was excited at wavelength $\lambda=230$ nm by a Nd:YAG laser. From figure, it is clear that a strong emission peak at around 3.20 eV ($\lambda = 388$ nm) and its second order at around 2.67 eV ($\lambda=465$ nm) are observed. The energy value of 3.20 eV corresponds to the direct band gap of LTA crystal. This optical band gap value is slightly less than that measured by conventional absorption spectroscopy

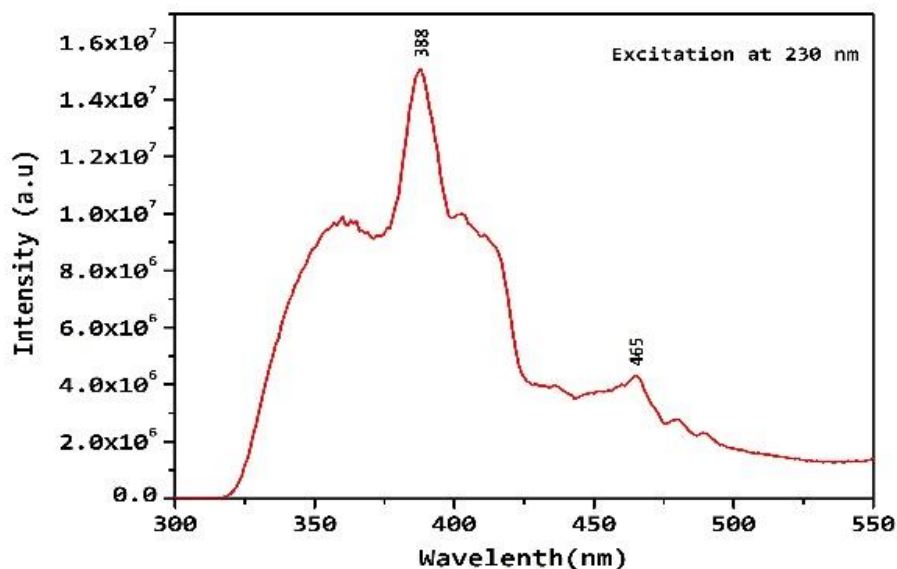


Fig. 3.4 PL spectrum of the as-grown LTA single crystal

technique [3.17]. Furthermore, the emission peak exhibits a broad and asymmetric profile. This behavior indicates the existence of several transitions below the conduction band or may be due to the overlap of various emission peaks. This is most likely associated with the presence of defects inside the band gap, probably due to oxygen vacancies [3.16]. The PL results indicate that the as-grown crystal has blue and green fluorescence emission and can be used as blue as well as green lasers.

3.3.4 Etching Study

It is well known fact that the defects in the crystals may destroy the mechanical, optical and electrical properties, which affect the usefulness of the crystals for device applications. The nonlinear optical properties, laser damage threshold etc., depends on the crystalline perfection of the crystals. Etching is one of the most selective characterization technique to identify the defects in the grown crystals and useful in obtaining the structural perfection and growth features of a grown crystal. This study was carried out on the grown LTA single crystal and a mixture of water and acetone was used as an etchant for 10, 20, 30, 40 and 50s after that it was wiped with tissue paper and then its surface was analyzed with the help of optical microscope in the reflection mode.

Fig. 3.5 shows the surface features of the as grown and etched LTA crystals with the mixture of water and acetone for 10, 20, 30, 40 and 50s respectively. It is clear from figure that the surface of the as grown crystal is having very less defects while the etched crystals surface is having identical rectangular etch pits in shape. The etch pits pattern remains same but the size of etch pits increases with increasing the etching time. The etch pits in the grown crystal is giving an indication to the initial dislocations formed at low angle boundaries or segregation of impurities.

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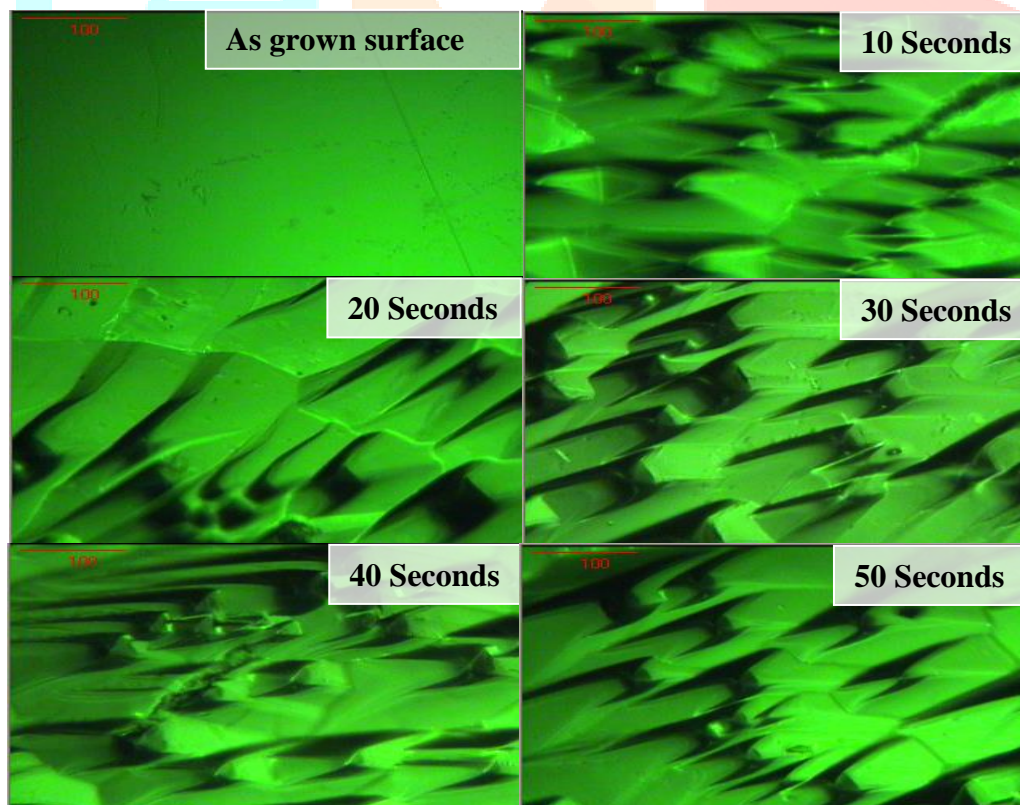


Fig.3.5 Etching photographs of the as-grown LTA single crystal at different time intervals

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