3. OPTICAL, THERMAL AND MECHANICAL MEASUREMENTS

We deal with here, in this Chapter, the optical, thermal and mechanical measurements carried out in the present study. The methods of the analyses are also dealt with briefly in this chapter.

Once a crystal is grown, often with beautiful external shapes, it is quite interesting to find its identity and chemical composition. For a more detailed and thorough understanding of the material, information about its purity, crystallinity, crystal structure and crystal perfection is required. The occurrence of lattice defects or the inclusion of impurities in a solid can give rise to optical absorption. The origin of such absorption is either the excitation of vibrational modes or the promotion of electrons from given set of energy states to others of higher energy. Similar effects occur in perfect crystals too. The most prominent features of the absorption spectrum of a solid are characteristics of the host lattice and impurity absorption bands are usually observable only if they occur in those spectral regions in which the host material is transparent. The emission of light from solids, on the other hand, is usually dominated by impurities even when their density is low as 1 in $10^6$. Thus a solid can absorb photons of some energy due to electronic transition characteristics of the host lattice and in consequence emit photons of a different (usually lower) energy corresponding to a transition between impurity energy levels. The optical properties of solids are of considerable technological importance. One of the many striking developments of the few decades has been the extension of optical techniques and relatively high resolution spectroscopy throughout the spectral range from visible
light to microwaves. The properties of a medium depend upon the intensity of radiation. The basis for this conclusion is that the field strength of the conventional light sources used before the advent of lasers, were much smaller than the field strengths of atomic and inter-atomic fields. The latter are of the order of $10^7$ to $10^{16}$ V/cm; whereas the former would not exceed atomic fields to the extent of changing the optical parameters. The high degree of coherence of the laser radiation has made it possible to generate 1 mW pulses, lasting a few tenths of nanoseconds, using moderately powerful lasers. At high fields, the relationship between the electric polarization $P$ and the field strength $E$ ceases to be linear and some interesting nonlinear effects come to force. Nonlinear properties in optical region have been strikingly demonstrated by harmonic generation of light.

In an insulator, the electrons are so tightly bound to the atoms that at ordinary temperatures they cannot be dislodged either by thermal vibrations or with ordinary fields. The negative and positive charges in each part of the crystal can be considered to be centered at the same point, and since no conductivity is possible, the localized charges remain that way essentially forever. When an electric field is applied to the crystal, the centers of the positive charges are slightly displaced in the opposite direction. This produces local dipoles throughout the crystal and the process of inducing such dipoles in the crystal is called polarization. The dipole moment induced in unit volume of a polarized insulator can be considered as the average of the dipole moments of all the atoms in that unit volume, and the ratio of the induced dipole moment to the effective field is called the polarizability of the atom. It is possible that certain groups of atoms already possess permanent dipole moments. In crystals
containing such atomic groups, an external field has the effect of orienting the dipoles parallel to the field direction.

The induced polarization or the delocalization of the electrons plays an important role in the interaction of light with some materials. In the present work, the optical characterizations made are:

(i) UV-Vis absorption spectral measurement,
(ii) Second harmonic generation (SHG) studies

3.1 UV-Vis spectrometry

Ultraviolet – visible (UV-Vis) spectroscopy or ultraviolet visible spectrometry involves the spectroscopy of photons and spectrophotometry. It uses light in the visible and adjacent near ultraviolet ranges. In this region of energy space molecules undergo electronic transitions.

When a beam of electromagnetic radiation strikes an object it can be absorbed, transmitted, scattered, reflected or it can excite fluorescence. The processes concerned in the absorption spectroscopy are absorption and transmission. The condition under which sample is examined for absorption is chosen to keep reflection, scatter and fluoresces to a minimum. An optical spectrometer records the wavelength at which absorption occurs together with the degree of absorption at each wavelength. Ultraviolet and visible spectroscopy is used for quantitative analysis of the samples.

The absorption of radiation in a sample follows the Beer-Lambert law which states that the concentration of a substance in a sample (thin film/ solution) is directly proportional to the absorbance “a”. As shown in the schematics of a spectrometer in Figure 25 “I₀” is the incident radiation, “I” is the intensity of transmitted radiation.
Absorbance \( (a) = \text{constant} \times \text{concentration} \times \text{cell length} \).

Mathematically, absorbance is related to percentage transmittance \( T \) by the expression,

\[
A = \log_{10}(I_0/I) = \log_{10}(100/T) = KCL
\]

Where “\( L \)” is the length of the radiation path through the sample “\( C \)” is the concentration of absorbing molecules in that path and “\( K \)” is the extinction coefficient that depends upon the nature of the molecule and wavelength of incident radiation. Absorbance is sometimes referred to as “extinction” or “optical density” also.

![Diagram of components of a typical UV-Vis spectrometer](image)

**Figure 25: A diagram of components of a typical UV-Vis spectrometer**

The UV-Vis spectral range is approximately 190-900 nm. It also spans the range of human visual acuity of approximately 400-750 nm, making UV-Vis spectroscopy useful in characterizing the absorption, transmission, and reflectivity of
a variety of technologically important materials such as pigments, coatings, windows, and filters [153]. Materials that can be characterized by UV-Vis spectroscopy include semiconductors for electronics, lasers and detectors; transparent or partially transparent optical components; solid-state laser hosts; optical fibers, waveguides, and amplifiers for communication; and materials for solar energy conversion. The use of UV-Vis spectroscopy in materials research can be divided into two main categories: (1) quantitative measurement of an analyte in the gas, liquid, or solid phase, and (2) characterization of the optical and electronic properties of a material.

Figure 26: Photograph of Vario Cary 500 scan spectrophotometer

In the present study, the UV-Vis absorption spectra for all the thirteen crystals grown were recorded in the wavelength range 200-800 nm using Vario Cary 500 scan spectrophotometer a photograph of which is shown in Figure 26. Aqueous solutions were used for the measurement.
3.2 The SHG Analysis

Growth of large single crystal is a slow and difficult process. Hence it is highly desirable to have some technique of screening crystal structures to determine whether they are non-centrosymmetric and to know whether they are better than those currently known. Such a preliminary test should enable us to carry out the activity without requiring oriented samples. Kurtz and Perry [154] proposed a powder SHG method for the comprehensive analysis of the second order nonlinearity. Employing this technique they surveyed a very large number of compounds. The nonlinear optical property of the grown single crystal is tested by passing the output of Nd:YAG Quanta ray laser through the crystalline powder sample.

A Q-switched, mode locked Nd:YAG laser was used to generate about 10.8 mJ/pulse at the 1064 nm fundamental radiation. This laser can be operated in two modes. In the single shot mode the laser emits a single 8 ns pulse. In the multishot mode the laser produces a continuous of 8 ns pulses at a repetition rate of 10 Hz. In the present study, a single shot mode of 8 ns laser pulse with a spot radius of 1mm was used. This experimental setup used a mirror and a 50/50 beam splitter (BS) to generate a beam with pulse energies about 10.9 mJ. The input laser beam was passed through an IR reflector and then directed on the micro crystalline powdered sample packed in a capillary tube of diameter 0.154 mm. The photodiode detector and oscilloscope assembly measured the light emitted by the sample. Microcrystalline powder of Urea was taken in a similar capillary tube sealed at one end for comparison. The intensity of the second harmonic output from the sample was compared with that of urea. Thus the figure of merit of SHG of the sample was estimated.
3.3 Thermal Analysis

Heat may be used as reagent. Taken through a wide range of temperature, a substance may undergo physical and chemical changes, react with the ambient atmosphere. All changes are accompanied by the absorption or release of energy in the form of heat. Some changes involve a weight gain or loss, and there may be thermo mechanical or electrical conductivity changes. The rate and temperature at which materials undergo physical and chemical transitions as they are heated and cooled, and the energy and weight changes involved is the subject of thermal analysis.

3.3.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis provides the analyst with a quantitative measurement of any weight change associated with a transition. For example, TGA can directly record the loss in weight with time or temperature due to dehydration or decomposition. Thermogravimetric curves are characteristic for a given compound or system because of the unique sequence of physico-chemical reactions which occur over definite temperature ranges and at rates that are a function of the molecular structure. Changes in weight are a result of the rupture bonds at elevated temperatures that lead to the evolution of volatile products or the formation of heavier reaction products. From such curves data are obtained concerning the thermodynamics and kinetics of the various chemical reactions, reaction mechanisms, and the intermediate and final reaction products.

In Differential Thermogravimetric Analysis (DTA) the actual measurement signal appears as a derivative plot of the weight loss or gain which aids in the accurate
assignment of the end beginning points of overlapping fractions which often appear as combined peaks in TGA.

For TGA, the sample is continuously weighed as it is heated to elevated temperatures. Samples are placed in a crucible or shallow dish that is attached to an automatic-recording balance. The automatic null-type balance incorporates a sensing element which detects a deviation of the balance beam from its null position. One transducer is a pair of photocells, a slotted flag connected to the balance arm, and a lamp (see Figure 27).

![Figure 27: Schematic diagram of TGA equipment with optical sensor](image)

Once an initial balance has been established any change in sample weight causes the balance rotate. This moves the flag so that the light falling on each photocell is no longer equal. The resulting nonzero signal is amplified and feedback as a current to a taut-band toque motor (the pivot point of the balance) to restore the
balance to equilibrium. This current is proportional to the weight change and is recorded on the y-axis of the recorder. Changes in mass can also be detected by contraction or elongation of a precision helical spring and is detected by the movement of an attached core in a linear variable differential transformer (see Figure 28) with either type balance. The sample container is mounted inside a quartz or pyrite housing which is located inside the furnace.

Figure 28: Modular diagram of TGA equipment with spring and transducer coil as sensor
Furnace temperature is continuously monitored by a thermocouple whose signal is applied to the X-axis of the recorder. In differential thermogravimetry the actual measurement signal is derived from a solid-state resistance-capacitance circuit which uses the direct output of the electrical weight-change signal from the thermobalance for the derivative, $\Delta w/\Delta t$, which is used in kinetic interpretations. The usual temperature range for TGA is from ambient to 1200 °C. Sample size ranges from 1 to 300 mg, and sensitivities down to a few micrograms of weight change are common.

### 3.3.2 Differential thermal analysis (DTA)

In differential thermal analysis (DTA) the temperature of a sample and a thermally inert reference material are measured as a function of temperature. Any transition which the sample undergone will result in liberation or absorption of energy by the sample with a corresponding deviation of its temperature from that of the reference. This differential temperature ($\Delta T$) versus the programmed temperature ($T$) at which the whole system is being changed tells analyst the temperature at which the transition occurs and whether the transition is exothermic or endothermic.

Typical DTA equipment is illustrated in Figures 29 and 30. The furnace contains a sample block with identical and symmetrically located chambers. Each chamber contains a centered thermocouple. The sample is placed in one chamber and the reference material, such as $\alpha$-Al$_2$O$_3$ is placed in the other chamber. The furnace and sample block temperature are then increased at a linear rate, most often 5 to 12 °C per minute, either by increasing the voltage through the heater element by a motor-driven variable transformer or by a thermocouple – actuated feedback type of controller.
The difference in temperature between sample and reference (S>R) thermocouples, connected in series-opposition, is continuously measured. After amplification (about 1000 times) by a high gain, low noise, DC amplifier for the microvolt-level signals, the difference signal is recorded on the y-axis of a millivolt recorder. The temperature of the furnace is measured by a separate thermocouple which is connected to the x-axis of the recorder, frequently through a reference ice junction or room-temperature compensator. Because the thermocouple is placed directly in the sample, or attached to the sample container, the DTA technique provides the highest thermometric accuracy of all of the thermal methods [121, 124, 125].
The temperature range is between 20 and 750 °C. Sample sizes range from 0.1 to 100 mg in DTA. By using a suitable pressure container, this technique may be extended to pressures up to 1000 psi and down to $10^{-5}$ for range.

Figure 31: Thermal analyser- simultaneous TGA/DTA TA Instrument Model SDT Q600
In the present study TGA and DTA measurements have been carried out using the thermal analyser- simultaneous TGA/DTA TA instrument Model SDT Q600 a photograph is (shown in Figure 31) for four samples LAA, LAAF4, LAAF4, LAAH4, and LAAO4 (maximum molar concentration of the dopants).

3.3.3 DSC measurements

In power- compensated DSC, the sample and a reference material are maintained at the same temperature ($\Delta T = T_s - T_r = 0$) throughout the controlled temperature programme. Any energy difference in the independent supplies to the sample and reference is then recorded against the programme temperature. The apparatus is shown schematically in Figure 32(a), and an example of a resulting DSC curve in Figure 32(b). There are many similarities between DSC and DTA, including the superficial appearance of the thermal analysis curves obtained, but the principle of power-compensated DSC is distinctly different to that of calorimetric DTA, also known as heat – flux DSC.

Thermal events in the sample thus appear as deviations from the DSC baseline, in either an endothermic or exothermic direction, depending upon whether more or less energy has to be supplied to the sample relative to the reference material. Again, these directions should be clearly marked on the reference material. Again, these directions should be clearly marked on the record, to avoid later confusion. In DSC, endothermic responses are usually represented as being positive, (i.e) above the baseline, corresponding to an increased transfer of heat to the sample compared to the reference. Unfortunately this is exactly the opposite convention to that usually used in DTA, where endothermic responses are represented as negative temperature
differences, below the baseline as the sample temperature lags behind the temperature of the reference[155].

The operating temperature range of power-compensated DSC instruments is generally more restricted than that of DTA instruments. The perkin-Elmer DSC-2 (see Figure 33), for example, has a maximum temperature of 726 °C (999 K).

Figure 32: Differential scanning calorimetry (DSC) (a) apparatus (S=sample: R=reference) (b) typical DSC curve (Note the DSC convention, which is opposite to the DTA convention, that an endothermic response is represented by a positive, i.e. upward peak)
3.4 Microhardness Measurements

Hardness is an important factor in the choice of ceramics for abrasives, bearings, toolbits, wear resistance coatings, etc. Hardness is a measure of resistance against lattice destruction or the resistance offered to permanent deformation or damage. Measurement of hardness is a nondestructive testing method to determine the mechanical behaviour of the materials. As pointed out by Shaw in 1973 [156], the term hardness is having different meanings to different people depending upon their area of interest. For example, it is the resistance to wear for a lubrication engineer and a measure of flow stress for a design engineer. All these actions are related to the
plastic stress of the material. For hard and brittle materials, the hardness test has proved to be a valuable technique in the general study of plastic deformation [157].

The hardness depends not only on the properties of the materials under test but also largely on the conditions of measurement. Microhardness tests have been applied to fine components of clock and instrument mechanisms, thin metal strip, foils, wires, metallic fibers, thin galvanic coatings, artificial oxide films, etc as well as the thin surface layers of metals which change their properties as a result of mechanical treatment (machining), rolling, friction and other effects. The microhardness method is widely used for studying the individual structural constituent elements of metallic alloys, minerals, glasses, enamels and artificial abrasives.

3.4.1 Methods of hardness testing

The various methods using which hardness measurement can be carried out are classified as below:

(i) Static indentation test
(ii) Dynamic indentation test
(iii) Scratch test
(iv) Rebound test
(v) Abrasion test

The most popular and simplest test is the static indentation test, wherein an indentor of specific geometry is pressed into the surface of a test specimen under a known load. The indentor may be a ball or diamond cone or diamond pyramid. A permanent impression is retained in the specimen after removal of the indentor. The hardness is calculated from the area or the depth of indentation produced. The vaiable
is the type of indentor or load. The indentor is made up of a very hard material to prevent its deformation by the test piece, so that it can cover materials over a wide range of hardness. For this reason, either an indentor of steel sphere or a diamond pyramid or cone is employed. A pyramid indentor is preferred as geometrically similar impressions are obtained at different loads. In this static indentation test, the indentor is pressed perpendicularly to the surface of the sample by means of an applied load. By measuring the cross sectional area or depth of the indentation and knowing the applied load, empirical hardness number may be calculated. This method is followed in Brinell, Meyer, Vickers, Knoop and Rockwell tests [158,159,160].

In the dynamic indentation test, a ball or a cone (or a number of small spheres) is allowed to fall from a definite height and the hardness number is obtained from the dimensions of the indentation and the energy of impact.

The scratch test can be classified into two types:

i) Comparison test, in which one material is said to be harder than another, if the second material is scratched by the first; and

ii) A scratch test is made with a diamond or steel indentor on the surface to a steady rate and under a definite load. The hardness number is expressed in terms of the width or depth of the groove formed.

iii) In the rebound test, an object of standard mass and dimension is bounced from the test surface and the height of rebound is taken as the measure of hardness. In the abrasion test, a specimen is loaded against a rotating disk and the rate of wear is taken as a measure of hardness.
3.4.2 Vickers test

Vickers hardness method is the reliable and most common among the various methods of hardness measurement discussed above. In this method, micro-indentation is made on the surface of a specimen with the help of diamond pyramidal indentor shown in Figure 34. It has been proposed that a pyramid by substituted for a ball in order to provide geometrical similitude under different values of load [161].

![Vickers diamond pyramidal indentor](image)

**Figure 34: Vickers diamond pyramidal indentor**

The Vickers pyramid indentor whose opposite faces contained an angle \( \alpha = 136^\circ \) is the most widely accepted pyramid indentor. A pyramid indentor is suited for hardness tests due to the following reasons [162].

- The contact pressure for a pyramid indentor is independent of indent size.
- Pyramid indentors are less affected by elastic release than other indentors.
The base of the Vickers pyramid is a square and the depth of indentation corresponds to $1/7^{th}$ of the indentation diagonal. Hardness is generally defined as the ratio of the load applied to the surface area of the indentation. The Vickers hardness number $H_v$ of Diamond Pyramid Number (DPN) is defined as

$$H_v = \frac{2P\sin(\alpha/2)}{d^2}$$

Where $\alpha$ is the apex angle of the indentor ($\alpha = 136^\circ$). The Vickers hardness number is thus calculated using the relation

$$H_v = 1.8544P/d^2 \text{ kg-mm}^{-2}$$

Where $P$ is the applied load in kg and $d$ is the diagonal length of the indentation mark in mm. Hardness values are always measured from the observed size of the impression remaining after a loaded indentor has penetrated and has been removed from the surface.

Thus, the observed hardness behaviour is the summation of a number of effects involved in the material’s response to the indentation pressure during loading, in the final measurement of the residual impression.

3.5 Results and Discussion

3.5.1 UV-Vis spectra

The UV-Vis spectra of pure and doped LAA crystals were recorded in the wavelength range 200-800 nm using a Vario Cary 500 scan spectrophotometer. Figure shows the UV-Vis optical absorption spectra of pure and doped LAA crystals. The cut-off wavelengths as observed from the absorption spectra (Figure 35) are shown in
Table 8. Interestingly, in the region starting from 200 to 800 nm, the crystal has almost less than 0.2 unit of absorption. It is also seen that dopants added into the LAA crystals have increased the cutoff wavelength. There is no orderly variation in cutoff wavelengths with respect to the molar impurity concentrations in the crystal lattice.

Efficient nonlinear optical crystals have an optical transparency lower cutoff wavelengths between 200 and 400 nm [163]. UV cutoff wavelengths for some of the NLO materials reported are: L-arginine bis(trifluoroacetate) - 237 nm[92], L-arginine fluoride - 245 nm [105], L-arginine trifluoroacetate - 232 nm [90], L-arginine hydrochloride monohydrate - 220 nm [96], L-arginine tetrafluoroborate - 198 nm [111].

The cutoff values obtained for the grown crystals are comparable with the values obtained for prominent NLO materials mentioned above. From the lower cutoff wavelengths the band gap energies were calculated using the formula

\[ E_g = \frac{hc}{\lambda} \]

Where,

\[ h = \text{Plank’s constant} \times 10^{-34} \text{ m}^2 \text{ kg/s} \]

\[ c = \text{Velocity of light} \times 10^8 \text{ m/s} \]

\[ \lambda = \text{Lower cutoff wavelengths} \]

In the present work, UV-Vis spectral measurements were made for all the thirteen samples and the forbidden energy \( E_g \) was calculated and are given in Table 7.
Figure 35: The UV-Vis absorption spectra for pure and doped crystals
Table 7: The optical absorption edges forbidden energy gaps and SHG efficiencies observed

<table>
<thead>
<tr>
<th>Crystals</th>
<th>Absorption edge, ( \lambda ) (nm)</th>
<th>Forbidden energy gap, ( E_g ) (eV)</th>
<th>SHG efficiency (in Urea unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAA</td>
<td>236.36</td>
<td>5.20</td>
<td>0.81</td>
</tr>
<tr>
<td>LAAH1</td>
<td>234.63</td>
<td>5.30</td>
<td>0.69</td>
</tr>
<tr>
<td>LAAH2</td>
<td>230.30</td>
<td>5.39</td>
<td>0.78</td>
</tr>
<tr>
<td>LAAH3</td>
<td>232.90</td>
<td>5.33</td>
<td>0.89</td>
</tr>
<tr>
<td>LAAH4</td>
<td>232.04</td>
<td>5.35</td>
<td>0.84</td>
</tr>
<tr>
<td>LAAF1</td>
<td>232.90</td>
<td>5.33</td>
<td>0.91</td>
</tr>
<tr>
<td>LAAF2</td>
<td>229.44</td>
<td>5.41</td>
<td>0.68</td>
</tr>
<tr>
<td>LAAF3</td>
<td>233.77</td>
<td>5.32</td>
<td>0.62</td>
</tr>
<tr>
<td>LAAF4</td>
<td>237.23</td>
<td>5.24</td>
<td>0.81</td>
</tr>
<tr>
<td>LAAO1</td>
<td>238.09</td>
<td>5.22</td>
<td>0.69</td>
</tr>
<tr>
<td>LAAO2</td>
<td>241.66</td>
<td>5.14</td>
<td>0.58</td>
</tr>
<tr>
<td>LAAO3</td>
<td>239.83</td>
<td>5.18</td>
<td>0.88</td>
</tr>
<tr>
<td>LAAO4</td>
<td>231.17</td>
<td>5.37</td>
<td>0.85</td>
</tr>
</tbody>
</table>

The low absorption in the visible region confirms the suitability of the grown crystals for NLO applications. The transmittance window in the visible region and IR region enables good optical transmission of the second harmonic frequencies of Nd:YAG lasers. The results obtained indicate a non-systematic variation of forbidden energy gap with the molar concentrations of the dopants. This may be due to creation of additional dipoles oriented in random direction due to doping.
3.5.2 SHG efficiencies

Second harmonic generation test was conducted on the grown crystals using Kurtz and Perry technique. The micro crystalline powdered sample was packed in a capillary tube of diameter 0.154 mm. The powder sample, with an average size of 100-150 µm was illuminated with a Q-switched mode-locked Nd\(^{3+}\): YAG laser of pulse width 8 ns at wavelength of 1064 nm fundamental radiation for the SHG efficiency measurements. Microcrystalline material of urea of the same particle size was used for comparison.

When a laser beam of input of 0.69 J was passed through the samples, powder, the second harmonic output signal and calculated efficiencies obtained were shown in Table 7. The SHG efficiency of the grown crystals have no systematic variation in efficiency with molar concentrations of the dopants.

3.5.3 Thermal properties

The thermal stability of the four crystals (LAA, LAAF₄, LAAH₄, LAAO₄) were identified by thermogravimetric analysis (TGA) differential thermal analysis (DTA) and differential calorimetric analysis (DSC). The TGA/DTA analyses were carried out using SDT Q600 V8.3 Build 101 analyser for a temperature range 40 to 800°C in the air atmosphere. The TGA, DTA and DSC patterns obtained in the present study for the four crystals considered are shown in Figures.36-39.

The Results reveal that the decomposition of LAA starts at 204 °C. This is supported by the DTA analysis where the endothermic reaction is observed at 201 °C. The other decomposition temperature points are 306 °C, 407 °C, 523 °C and 590 °C.
It can be seen from the thermal analysis that LAA subjected to continuous heating remains stable up to 200 °C. Finally it decomposes completely forming a residue.

The DSC analysis for LAA is carried out between 20 and 750 °C in air atmosphere. Since there is no endo or exothermic transitions below 208 °C, the materials are proved to be stable in this region. The resistivity of the materials against thermal crack is evident as the DSC trace is smooth up to nearly 200 °C. It is the property observed for compounds where the lattice force is more predominating than the covalent bonding forces in molecules. It is also observed that the electrostatic force that originated as a result of perfect proton transfer between acetic acid and L-arginine becomes dominating to provide resistance to melting before decomposition [164].

The TGA/DTA curves obtained for LAFF4 shows that the decomposition of LAFF4 starts at 191 °C. When the crystal is further heated, the other decomposition points are 286, 457 and 586 °C and above 741 °C there is no prominent weight loss.

The DSC curve for LAFF4 also shows there is no endo or exothermic transitions below 211 °C, the material is proved to be stable in this region. It is found that the decomposition temperature of LAFF4 is decreased from that of pure LAA. This decrease is due to the decrease in bond energy by the addition of formate ions into the crystal lattice of pure LAA [102].
Figure 36: TGA/DTA and DSC curves of pure LAA
Figure 37: TGA/DTA and DSC curves of LAAF4

Figure 38: TGA/DTA and DSC curves of LAAH4
The TGA/DTA curves obtained for LAAH4 shows that the decomposition of LAAH4 starts at 204 °C. When the crystal is further heated, the other decomposition points are 301, 395 and 482 °C and above 567 °C there is no prominent weight loss.

The DSC curve for LAAH4 also reveals no endo or exothermic transition below 212 °C, the material is proved to be stable in this region. The resistivity of the material against thermal crack is evident as the DSC trace is smooth upto 212 °C. It is found that the decomposition temperature of LAAH4 has a small variation from that of the decompostition temperature of pure LAA. This small variation is expected due to the decrease in bond energy by the addition of chloride ions into the crystal lattice of pure LAA.
From the TGA/DTA curves it is observed that the decomposition of LAAF4 starts at 200 °C. When the crystal is further heated, the other decomposition points are 283, 400, 517 °C and above 581 °C there is no prominent weight loss.

The DSC curve for LAAO4 shows no endo or exothermic transitions below 210 °C, the material is proved to be stable in this region. The resistivity of the material against thermal crack is evident as the DSC trace is smooth up to 209 °C. It is found that the decomposition temperature of LAAO4 is decreased from that of pure LAA. This decrease is due to the decrease in bond energy by the addition of oxalate ions into the crystal lattice of pure LAA.

The major weight loss which occurs in low temperature region begins around 200 °C and ends around 600 °C. Table 8 shows the decomposition temperature observed. The residue that remains after all the decomposition process is expected to be only carbon mass.

**Table 8: Decomposition temperatures of the crystals subjected to thermal measurements**

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Decomposition temperature(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAA</td>
<td>204</td>
</tr>
<tr>
<td>LAAF4</td>
<td>191</td>
</tr>
<tr>
<td>LAAH4</td>
<td>204</td>
</tr>
<tr>
<td>LAAO4</td>
<td>200</td>
</tr>
</tbody>
</table>

**3.5.4 Mechanical properties**

In the present work, the hardness number and work hardening coefficient of all the crystals namely LAA, LAAF1, LAAF2, LAAF3, LAAF4, LAAH1, LAAH2,
LAAH3, LAAH4, LAAO1, LAAO2, LAAO3 and LAAO4 have been determined. LAA is one of the best nonlinear optical crystals suited for second harmonic generators. For the fabrication of second harmonic crystals, many well prominent planes are required. Such fabrication requires a bulk crystal of a wide plane. Many crystals crack or break during cutting, lapping and polishing. To avoid this, a number of crystal pieces are tried during preparation of samples for characterization so that at least a few remain good for the final electroding of the surface. During fabrication of SHG generators, if the crystal is fragile, it easily breaks and many number of crystal pieces are wasted. Hence, it is understood that crystals of wide plane of higher hardness are necessary for device fabrication.

The hardness numbers ($H_v$) observed in the present study are given in Table 9. Figure 40 shows the plots of load ($P$) versus Vicker’s hardness number ($H_v$) for the 13 grown crystals. It is observed that the Vicker’s hardness number increases with the increase in load. In all the grown crystals the increase in the hardness with load can be attributed to the work hardening of the surface layers. Beyond the load of 100 g, significant cracking occurs around the indentation mark, which may be due to the release of internal stress generated locally by indentation. Out of all the samples the impurity added ones are found to be weaker than the pure one. Generally, the hardness of the material is related to its bonding and its crystallographic orientation. The dopants added LAA crystals have lower hardness values when compared to that of the hardness value of pure LAA. Also it is found that the hardness number is found to be varying with the variation in the concentration of the dopant in the lattice of the crystals. But the variation is not systematic.
Figure 40: The plots of Vicker’s hardness number (H, kg/mm²) versus load (P(g))

The plots of log d against log P for all the grown crystals are shown in Figure 41. The values of work hardening exponent calculated from slope of the straight lines are determined using least square fit method and the values of “n” are provided in Table: 9.
Figure 41: Log P versus Log d plots
Table 9: Microhardness data for all the crystals grown

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Microhardness number ($H_v$) for a load of</th>
<th>Work hardening coefficient(n)</th>
</tr>
</thead>
<tbody>
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The work hardening coefficient “n” of all the crystals are found to be greater than 2, hence the materials are said to be soft ones.

According to Onitsch, if n>2 the materials are said to be soft ones [165]. He also found that microhardness increases with increasing load when n>2 and decreases with increasing load when n<2. The increase in $H_v$ for increasing load observed in the present study is in good agreement with the theoretical prediction.