CHAPTER 3

GROWTH OF LANTHANUM CALCIUM BORATE (LCB) SINGLE CRYSTALS FROM MELT AND ITS CHARACTERISATION

3.1 INTRODUCTION

The vital applications of non-linear optical (NLO) single crystals for second harmonic generation (SHG), sum or different frequency mixing, optical parametric oscillation or amplification have resulted in the development of many new inorganic NLO single crystals. Over the past, the search for new and better NLO materials has never stopped in the endeavor to develop new laser sources and its extended application in current scenario. As a result, one of the very useful ultraviolet (UV) NLO material, K(B$_5$O$_6$ (OH)$_4$). 2H$_2$O (KB5) is the first inorganic NLO crystal discovered in the borate series of materials. Research on borate based crystals was intensified after the invention of β-BaB$_2$O$_2$ (BBO). Also, a series of borate crystals were developed like CsB$_3$O$_5$ (CBO), CsLiB$_6$O$_{10}$ (CLBO), YCa$_4$O (BO$_3$)$_3$ (YCOB), GdYCOB, LCOB, Nd:LCOB and K$_2$Al$_2$B$_2$O$_7$ (KAB) which were grown by TSSG and Czochralski techniques. Growth of YCOB crystals by employing flux method for the first time was also reported (Arun Kumar et al 2008, Arun Kumar et al 2009). A detailed review of the above mentioned borate crystals were reported (Petra Becker 1998, Sasaki et al 2000). Borate crystals are mainly concentrated due to its relatively high resistance against laser-induced damage and higher transparency in the UV region, and often used for high-power UV light.
In the present investigation, the growth of LCB single crystals was carried out using Czochralski technique. This chapter discusses about the synthesis of LCB polycrystalline compound and the growth of LCB single crystals and its various characterization results to analyse the properties of the grown crystals.

### 3.2 LANTHANUM CALCIUM BORATE – A BRIEF INTRODUCTION

In the past few years several new rare-earth (R) calcium borates such as $\text{RCa}_4\text{O(BO}_3\text{)}_3$, $\text{R}_2\text{CaO(BO}_3\text{)}_2$, and $\text{RCaB}_7\text{O}_{13}$ have been synthesized (Khamaganova et al 1991, Norrestam et al 1992, Chen et al 1988) in the ternary system $\text{R}_2\text{O}_3$-$\text{CaO}$-$\text{B}_2\text{O}_3$. Among them, $\text{RCa}_4\text{O(BO}_3\text{)}_3$ has attracted considerable interest as a potential material for nonlinear optical (NLO) applications because it exhibits a relatively large second-harmonic generation (SHG) effect (Aka et al 1997), and the single crystal is easily grown (Iwai et al 1997). Among many NLO borate crystals, Lanthanum Calcium Borate is a new class of rare-earth borates of composition $\text{R}_2\text{CaB}_{10}\text{O}_{19}$ with a powder SHG effect as large as that of $\text{RCa}_4\text{O(BO}_3\text{)}_3$ (Wu et al 1998) is one of the new NLO materials which were reported by Wu et al (Yicheng Wu et al 2001).

The LCB compound crystallizes in a non-centro symmetric space group, a basic condition for a potential harmonic generation material. A model called the “anionic group theory” was designed by Chen and his co-workers and is used to understand the relation between composition, structure of borate materials, and the related NLO properties (Chen 1993). The nonlinearity of a borate crystal originates in the boron-oxygen groups, so borates containing BO$_3$ groups or more complex groups made of BO$_3$ triangles such as B$_3$O$_7$, B$_3$O$_8$, and B$_5$O$_{12}$ groups could be expected to possess a SHG effect 2-3 times larger than that of KDP. And in fact, LCB was found to have a powder SHG effect about twice as large as that of KDP.
The polyhedral representation of the structure of LCB is shown in Figure 3.1 (Yicheng Wu 2001). The structure contains the infinite two-dimensional double layers running almost perpendicular to the c axis of the crystal. The La atoms are located in layers, while the Ca atoms are located between two layers. The open circles represent La atoms, and the filled circles represent Ca atoms. The structure contains layers built up from \( \text{B}_5\text{O}_{12} \) double-ring pentaborate groups. The \( \text{B}_5\text{O}_{12} \) group is formed by three \( \text{BO}_4 \) tetrahedra and two \( \text{BO}_3 \) triangles with shared O atoms as shown in Figure 3.2(a). In this group, O(5) and O(7) atoms are shared with other \( \text{BO}_4 \) tetrahedra, while O(2), O(6), O(9), and O(10) atoms are shared with \( \text{BO}_4 \) tetrahedra and \( \text{BO}_3 \) triangles. \( \text{B}_5\text{O}_{12} \) groups are linked together to form an infinite two-dimensional double layer by sharing O(3) and O(4) atoms with one another. In this layer, upper and lower networks are connected by shared O(1) atoms. The layer runs almost perpendicular to the c axis of the crystal. The La atoms are located in layers, while the Ca atoms are located between two layers. The coordination environments of La and Ca atoms by O atoms are shown in Figure 3.2 (b).
The LCB is one of the biaxial crystals and the crystal crystallizes in the monoclinic system with space group C2. Some of the important crystal properties are listed in Table 3.1. LCB is one of the members of the newly discovered NLO Borate crystal RCB (R$_2$CaB$_{10}$O$_{19}$) family, where R represents rare-earth element. LCB possess very good NLO properties, suitable hardness, and high laser-induced damage threshold (> 11GW/Cm$^2$) and is insensitive to moisture.

**Table 3.1 Crystal properties of lanthanum calcium borate**

<table>
<thead>
<tr>
<th>S. No</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Formula</td>
</tr>
<tr>
<td></td>
<td>La$<em>2$CaB$</em>{10}$O$_{19}$</td>
</tr>
<tr>
<td>2.</td>
<td>Crystal Structure and space group</td>
</tr>
<tr>
<td></td>
<td>Monoclinic, C2</td>
</tr>
<tr>
<td>3.</td>
<td>Lattice Parameters</td>
</tr>
<tr>
<td></td>
<td>$a = 11.043(3)$ Å, $b = 6.563(2)$ Å, $c = 9.129(2)$ Å, $\beta = 91.47^\circ$</td>
</tr>
<tr>
<td>4.</td>
<td>UV Transparency range</td>
</tr>
<tr>
<td></td>
<td>220 - 3600 nm</td>
</tr>
<tr>
<td>5.</td>
<td>Melting Point</td>
</tr>
<tr>
<td></td>
<td>1048°C</td>
</tr>
<tr>
<td>6.</td>
<td>Hygroscopicity</td>
</tr>
<tr>
<td></td>
<td>Non-hygroscopic</td>
</tr>
<tr>
<td>7.</td>
<td>Hardness</td>
</tr>
<tr>
<td></td>
<td>6.5 Mohs</td>
</tr>
<tr>
<td>8.</td>
<td>Density (calculated)</td>
</tr>
<tr>
<td></td>
<td>3.665 g/cm$^3$</td>
</tr>
<tr>
<td>9.</td>
<td>Absorption Coefficient</td>
</tr>
<tr>
<td></td>
<td>6.886/mm</td>
</tr>
<tr>
<td>10.</td>
<td>Effective nonlinear coefficient</td>
</tr>
<tr>
<td></td>
<td>1.05 pm/V</td>
</tr>
</tbody>
</table>
3.3 METHODS USED TO GROW LCB SINGLE CRYSTALS

Lanthanum Calcium Borate single crystals can be grown using melt growth method by employing both by Top-Seeded Solution Growth (TSSG) technique and by crystal pulling method using Czochralski technique. The detailed phase diagram of La₂O₃-CaO-B₂O₃ is not available for the LCB compound. The phase relationship in the binary system of LaB₃O₆-CaB₄O₇ were investigated (Yicheng Wu et al 2003) and is reported that the LCB single crystals can also be easily grown from the melt close to stoichiometric composition. For the growth of LCB using TSSG, CaB₄O₇ was used as the flux (Junxin Wang et al 2002). Also, CaO-Li₂O-B₂O₃ flux system was used for the growth of LCB crystals by flux method and the different flux ratios of CaO-Li₂O-B₂O₃ were reported (Fangli Jing et al 2005, Fangli Jing et al 2006). Single crystals of LCB were also grown by using the stoichiometric melt growth method (Xu et al 2002).

3.4 SYNTHESIS OF POLYCRYSTALLINE LCB MATERIALS

The synthesis of polycrystalline materials of LCB were prepared by using the 3N purity chemicals. The stoichiometric ratio of lanthanum oxide La₂O₃, calcium carbonate CaCO₃ and boric acid H₃BO₃ were taken and mixed well using an agate mortar. The synthesis procedure was carried out in two step process as reported (Xu et al 2002). Firstly, the stoichiometric mixture was taken in 100cc platinum crucible and was kept at a temperature of 450 °C for 12 h to eliminate the absorbed water content and to decompose the carbonate present in the mixture. After cooling to room temperature, the mixture was once again well grounded. Secondly, the product was annealed at 930 °C for 36 h to enable the solid state reaction and for the formation of LCB compound.
The synthesis reaction is given by the following chemical equation (3.1),

\[
\text{La}_2\text{O}_3 + \text{CaCO}_3 + 10 \text{H}_3\text{BO}_3 \rightarrow \text{La}_2\text{CaB}_{10}\text{O}_{19} + \text{CO}_2 + 15\text{H}_2\text{O}
\]  

(3.1)

3.5 SINGLE CRYSTAL GROWTH

The bulk crystal growth process was carried out by melt growth process using Czochralski technique. For the growth of LCB single crystals, BCG01 model precision pulling head as shown in Figure 3.3 is fitted with home made growth assembly. The installed crystal pulling head has the precision for the rotation rate and translation rate as low as 1rpm and 0.1mm/hr respectively for slow growth speed. For fast growth, maximum of 35rpm and 72mm/hr respectively can be made. The rotation and translation controller are as shown in Figure 3.4. Indigenously built two zone electrical grooved muffle furnace made of Kanthal heating element as shown in Figure 3.5 was used to melt the LCB compound. Eurotherm temperature controller and programmer of model 2604 were used to control the two zone furnace assembly.

The temperature profile of the two zone furnace was taken for the growth temperature and tested for the bulk LCB single crystal growth. The synthesized material of LCB was melted at 1048°C. Further the temperature was increased to 1080°C for homogenization of the melt. After cooling to 1065°C at the rate of 1°C/hr, the melt was soaked at 1065°C for 12 h. The LCB crystal was grown in a resistance heated tube furnace by Czochralski method. The growth parameters are: Pulling rate – 0.2mm/hr, rotation rate varied between 05 – 10 rpm, cooling rate during crystal growth is varied between 0.1 – 0.3°C/hr, seed – platinum wire as shown in Figure 3.6, container - platinum crucible with capacity of 100 cc with the size of 50mm in
diameter and 50mm in height was used. The as grown crystals from melt are shown in Figure 3.7.

Figure 3.3  Precision pulling head

Figure 3.4  Rotation and translation controllers of precision pulling head
Figure 3.5. Two zone electrical grooved muffle furnace

Figure 3.6 Platinum wire used as seed for LCB growth
3.6 CHARACTERISATION

The assessment of the quality of the crystals and its properties that are grown using different methods will be revealed only when the grown crystals were subjected to different characterization tools. For the structural property analysis, X-ray diffraction technique is widely used for studying crystalline materials (Cullity 1978). Optical studies such as UV-VIS-NIR and FTIR were also performed on the grown crystal. The grown crystals were subjected to various characterization studies to find its structural, thermal, optical, dielectric, surface and NLO properties.

3.6.1 X-Ray Diffraction Analysis

The synthesized polycrystalline LCB powder was analysed by powder X-ray diffraction studies using Rich Seifert diffractometer with CuKα radiation source (λ = 1.540 Å) at room temperature. The results of the powder XRD pattern for the synthesized polycrystalline LCB powder is shown in Figure 3.8. The indexed powder XRD pattern confirms the formation of
single phase LCB compound and the result is in accordance with previously reported (Xu et al 2002).

As grown LCB single crystal is subjected to single crystal X-ray diffraction analysis. The X-ray diffraction data of the LCB single crystal was collected using Enraf - Nonius CAD – 4 diffractometer, with graphite monochromated CuKα radiation source. From the single crystal XRD studies, it is observed that LCB crystal belongs to the monoclinic system, space group C2, with the lattice parameters of a = 11.042 Å, b = 6.561 Å, c = 9.126 Å and β = 91.49°. The results reveal that the obtained lattice parameters are in good agreement with the earlier reports (Yicheng Wu et al 2001).

3.6.2 FTIR Analysis

The grown crystal of LCB was subjected to FTIR analysis and the corresponding spectrum was recorded using KBR pellet method in the wave
number ranging from 400 – 4000 cm\(^{-1}\) and is shown in Figure 3.9. FTIR analysis was carried out to confirm the presence of functional groups and their vibration modes in the LCB crystals. The present investigation is in good agreement with the results obtained for other borates indicating the wave numbers of fundamental vibrations of \((\text{BO}_3)^3^-\) ions in the four distinct regions 1350-1200, 950-930, 790-730 and 680-590 cm\(^{-1}\) (Maczka et al 2004). The absorption peaks at 1250 cm\(^{-1}\), 1067 cm\(^{-1}\) and 957 cm\(^{-1}\), are due to the asymmetric and the symmetric stretching modes of \((\text{BO}_3)^3^-\) ions. The absorption peaks at 810 cm\(^{-1}\) and 717 cm\(^{-1}\) are due to the symmetric and the asymmetric bending modes of \((\text{BO}_3)^3^-\) ions. The absorption peak at 515 cm\(^{-1}\) is due to the internal vibration of La-O bond. Hence, all the possible peaks of the LCB crystal are present in the FTIR spectrum.

![Figure 3.9 FTIR spectrum of LCB compound](image-url)
3.6.3 EDAX analysis

EDAX analysis was carried out to find out the constituent elements present in the as grown LCB crystal sample. For this analysis, Hitachi S-3400N instrument was used to record the EDAX spectrum. The presence of the constituent elements of the LCB crystal was confirmed by the occurrence of their respective peaks in the recorded spectrum as shown in Figure 3.10 and the presence of the elements and its proportions are presented in Table 3.2.

![EDAX spectrum of LCB](image)

**Figure 3.10 EDAX spectrum of LCB**

**Table 3.2 The presence of the constituent elements of the LCB crystal**

<table>
<thead>
<tr>
<th>S.No</th>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Formula</th>
<th>Compound %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Boron</td>
<td>15.58</td>
<td>39.45</td>
<td>B</td>
<td>15.58</td>
</tr>
<tr>
<td>2.</td>
<td>Oxygen</td>
<td>26.84</td>
<td>45.91</td>
<td>O</td>
<td>26.84</td>
</tr>
<tr>
<td>3.</td>
<td>Calcium</td>
<td>6.78</td>
<td>4.63</td>
<td>Ca</td>
<td>6.78</td>
</tr>
<tr>
<td>4.</td>
<td>Lanthanum</td>
<td>50.80</td>
<td>10.01</td>
<td>La</td>
<td>50.80</td>
</tr>
</tbody>
</table>
3.6.4 Thermal Analysis

The synthesized polycrystalline powder of LCB materials was taken and the thermal analysis was performed using NETSZCH – GmbH thermal analyzer in nitrogen atmosphere at a heating rate of 10 °C/min. The differential thermal curve for LCB shows an endothermic peak associated with the melting of LCB at 1048 °C which is in comparable with that of the reports (Yicheng Wu et al 2001). The obtained DTA graph is shown in Figure 3.11.

![Figure 3.11 DTA curve of LCB compound](image)

3.6.5 UV-VIS-NIR Analysis

NLO material can be used in optical devices only if it has a wide transparency range. So transmission spectra are very important for all the NLO materials. To find the transmission range of LCB crystals, the UV-VIS-NIR spectral transmittance was recorded with an as-grown single crystal of LCB of 3 mm thickness in the wavelength range of 200-2500nm. The recorded transmission spectrum is shown in Figure 3.12. The lower cutoff
wavelength for the LCB crystal was less than 200 nm. The as-grown crystal was more than 50% transparent in the UV and visible regions.

![Figure 3.12 UV-VIS-NIR spectral graph of LCB crystal](image)

### 3.6.6 Specific Heat Studies

Specific heat is one of the important factors that influence the damage threshold of a crystal. Higher specific heat will have more resistance to laser damage, since a rise in temperature with laser irradiation is one of the mechanism by which the damage is caused (Fangli Jing 2008). The specific heat measurement was recorded for the LCB single crystal using a Perkin Elmer DSC-7 model instrument. The measurements were carried out in nitrogen atmosphere. The sample of 35mg was taken and is heated at the rate of 20 °C/min. The recorded spectrum is shown in Figure 3.13. Specific heat of LCB is measured in the temperature range from 55 °C to 550 °C. The calculated specific heat values are 0.666 J/g°C and 3.511 J/g°C at 55 °C and 550 °C respectively.
3.6.7 Dielectric Studies

The phenomena of nonlinear optics arise when the nonlinear polarization of the crystals with respect to the applied electric field. The polarization of the crystals with respect to the applied electric field forms the base for dielectric measurements. LCB crystals were subjected to dielectric studies to study the dielectric behaviour of the crystals. The crystal sample with a thickness of 7 mm was used for the analysis. Electronic grade silver paste was applied on the surfaces of the samples to ensure firm electrical contact. The experiment was carried out for different frequencies starting from 5 Hz to 5 MHz. The dielectric constant was calculated using the equation (3.2)

\[ \varepsilon_r = \left( \frac{Cd}{\varepsilon_0 A} \right) \]

(3.2)
where, $\varepsilon_r$ is the relative permittivity, $C$ is the capacitance, $d$ is the thickness of the crystal, $\varepsilon_0$ is the permittivity of free space and $A$ is the area of the crystal. Figures 3.14(a) and 3.14(b) show the variation of dielectric constant and loss for different frequencies of LCB single crystals at room temperature. From

**Figure 3.14** (a) Dielectric constant versus frequency graph and (b) Dielectric loss versus frequency graph of LCB
the curves it is observed that the dielectric constant and dielectric loss
decrease with the increasing frequencies and attains saturation at higher
frequencies. The low dielectric loss was consistent with nearly constant level
of dielectric constant over the wide frequency range. The low value of
dielectric loss indicates that the grown crystal contains minimum defects.
Crystals with low dielectric constant are more suitable for nonlinear optical
applications and crystals with higher dielectric constant lead to power
dissipation (Dalton 2003). Hence from the results it’s observed that the LCB
crystal is suitable for its usage in electro-optic applications

3.6.8  HRXRD Analysis

A multicrystal crystal X-ray diffractometer designed and developed
at National Physical Laboratory, New Delhi, India (Krishan Lal and
Bhagvannarayana 1989) was used to study the crystalline perfection of the
LCB single crystal. Figure 3.15 shows the schematic diagram of the
multicrystal X-ray diffractometer. The divergence of the X-ray beam
emerging from a fine focus X-ray tube (Philips X-ray Generator; 0.4 mm x
8 mm; 2kWMo) is first reduced by a long collimator fitted with a pair of fine
slit assemblies. This collimated beam is diffracted twice by two Bonse - Hart
(Bonse et al 1965) type of monochromator crystals and the thus diffracted
beam contains well resolved MoKα₁ and MoKα₂ components. The MoKα₁
beam is isolated with the help of fine slit arrangement and allowed to further
diffrac from a third (111) Si monochromator crystal set in dispersive
geometry (+, -, -). Due to dispersive configuration, though the lattice constant
of the monochromator crystal and the specimen are different, the dispersion
broadening in the diffraction curve of the specimen does not arise. Such an
arrangement disperses the divergent part of the MoKα₁ beam away from the
Bragg diffraction peak and thereby gives a good collimated and
monochromatic MoKα₁ beam at the Bragg diffraction angle, which is used as
incident or exploring beam for the specimen crystal. The dispersion phenomenon is well described by comparing the diffraction curves recorded in dispersive (+, -, -) and non-dispersive (+, -, +) configurations. This arrangement improves the spectral purity ($\Delta \lambda / \lambda \ll 10^{-5}$) of the MoK$_{\alpha 1}$ beam. The divergence of the exploring beam in the horizontal plane (plane of diffraction) was estimated to be $<< 3$ arc sec.

The specimen (LCB crystal) occupies the fourth crystal stage in symmetrical Bragg geometry for diffraction in (+, -, -, +) configuration. The specimen can be rotated about a vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.4 arc sec. The diffracted intensity is measured by using a scintillation counter. To provide two-theta ($2\theta_B$) angular rotation to the detector (scintillation counter) corresponding to the Bragg diffraction angle ($\theta_B$), it is coupled to the radial arm of the goniometer of the specimen stage. The rocking or diffraction curves were recorded by changing the glancing angle (angle between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position $\theta_B$ (taken as zero for convenience) starting from a suitable arbitrary glancing angle. The detector was kept at the same angular position $2\theta_B$ with wide opening for its slit to record the diffraction curve in $\omega$ scan mode.

Before recording the diffraction curve, the LCB crystal was first lapped and chemically etched in a non-preferential etchant to remove the non-crystallized solute atoms remained on the surface of the crystal and also to ensure the surface planarity. This process also ensures to remove surface layers. The diffraction curves recorded on the LCB crystal is as shown in Figure 3.16. The FWHM value of the diffraction curve is found to be 32 arc s, which indicates that the grown crystals were of good crystalline quality.
3.6.9 SEM Analysis

LCB single crystals were subjected to SEM Analysis using Hitachi S-3400N instrument to analyse the surface morphology of the as grown crystals. Figure 3.17 shows the surface SEM images of the LCB crystal. From the SEM image it is observed that the LCB crystal possess layer growth pattern.
3.6.10 Etching Studies

Etching of surfaces using desirable solvent gives more information about the surface features. Patterns observed on surfaces like spirals, hillocks, and slip pattern, etc., yield considerable information on the growth process and growth mechanism of the crystal. For this analysis, Olympus fluorescence microscope (model BX 41) in the normal optical microscope mode was employed to study the surface features of the as-grown crystal. Etching is the selective dissolution of the crystal, which is used to reveal the surface features (Sangwal 1987). To analyze the surface morphology, an as-grown transparent crystal was selected for the observation of etch patterns. The selected crystal was finely polished by gently rubbing with a fealty cloth wetted with 50% ethanol and 50% water and the final polishing was carried out using a thick wet cloth. Etching studies were carried out at room temperature using dilute nitric acid as the etchant for the duration of 3 minutes. Layer growth patterns were observed as shown in Figure 3.18.
3.6.11 Powder SHG Test

The fundamental beam with the wavelength of 1064 nm from a Q-switched Nd: YAG laser (Pro Lab 170 Quanta ray) was used to test the Second Harmonic Generation (SHG) property of the grown LCB single crystals by using the Kurtz powder technique (Kurtz and Perry 1968). The schematic of the experimental arrangement used to study the SHG test for the
LCB specimen is as shown in Figure 3.19. Pulse energy of 3.6 mJ/pulse with the pulse width of 8 ns and repetition rate of 10 Hz was used and 90° geometry was employed. The fundamental beam was filtered by using a monochromator. The Photo multiplier tube (Philips Photonics) was used as the detector. Based on the powder SHG test, it is observed that the measured powder SHG efficiency of LCB crystals was twice that of standard KDP which was employed as the reference material.

3.6.12 Laser Damage Threshold Studies

The LCB single crystals are non hygroscopic and the material posses higher transmission in the UV region (less than 200nm), it can be utilised in the laser systems for frequency conversion applications. It is very important that the crystal should be capable of withstanding for high power laser operations. The laser induced damage threshold (LDT) is a vital property for an optical crystal which will be employed in laser applications. The grown crystal can be used in high power lasers systems provided the crystal has a high LDT value. While subjecting the crystal for the high power laser irradiation, thermal effects build up on the crystal which leads to the damage of the crystal. The minimum amount of laser energy required to cause the damage is determined by the study. The value of the LDT varies with respect to the wavelength, pulse width, repetition rate of the incident beam for the same crystal itself.

The laser damage threshold value of LCB single crystals has been determined using a Q-switched Nd:YAG laser for 20 ns laser pulses at the wavelength of 1064 nm. The pulse repetition rate of 10 Hz was used. The laser beam divergence is 2 mrad. The output intensity of the laser is controlled with a variable attenuator and delivered to the test sample located near the focus of the converging lens. The spot size of the laser on the sample is fixed using a lens with a focal length of 20.5 cm. During laser radiation, power
meter was used to record the energy density of the input beam which is sufficient to damage the crystal. From the spot size of the beam, the radius of the beam (r) was estimated.

The energy density is the ratio of input energy of the incident laser beam to the area of the crystal which is irradiated by the beam. It is generally expressed in GW/cm$^2$. The input power can be calculated as the ratio of the laser pulse energy (mJ) to the time duration of the pulse (ns). Since the spot size is circular, area (A) can be calculated using the formula $\pi r^2$. Laser damage threshold value of the LCB crystal was found to be 11.7 GW/cm$^2$. The LDT result indicates that the grown LCB single crystals can be used in high power laser devices for frequency conversion applications.

3.7 CONCLUSION

Polycrystalline LCB compound was synthesized stoichiometrically. Lanthanum calcium borate single crystal was grown by melt growth technique. Formation of single phase LCB compound was confirmed by powder XRD, and FTIR analysis. From the single crystal XRD studies, crystal system and crystal parameters were determined. DTA analysis reveals that the compound melts congruently at 1048°C. EDAX analysis confirms the presence of all the constituent elements of LCB. UV-VIS-NIR spectral studies shows that the crystal posses a UV cut-off less than 200 nm with more than 55% transparent in the UV and visible region. The specific heat values recorded are observed to be good to operate in devices involving high temperatures. From the room temperature dielectric analysis, it is observed that both the dielectric constant and dielectric loss are low at higher frequencies. HRXRD curve with FWHM value of 32 arc s shows that the grown crystals were of good crystalline quality. Both SEM and etching analysis shows that the crystal possesses layer growth pattern. Powder SHG analysis shows that the compound is NLO active and the crystal possess good resistance against laser induced damage for device applications.