CHAPTER 5

GROWTH OF LCOB AND NdLCOB SINGLE CRYSTALS
FROM MELT AND THEIR CHARACTERIZATION

5.1 INTRODUCTION

In the series of rare earth calcium oxy borate (RECOB) crystals, reports on the growth and characterization of lanthanum calcium oxy borate crystals are lesser. The growth and characterization of LCOB single crystals and neodymium lanthanum calcium oxy borate crystals (NdLCOB) were performed and reported.

The lanthanum calcium oxy borate single crystals are good candidates for applications in the ultraviolet region, since the lanthanum ion has no absorbing peak in the UV wavelength range, and from the structure point of view as it possesses the monoclinic crystal structure with the space group $C_m$. Hence it can act as good NLO crystal for the realization of UV sources. The LCOB crystal offers suitable sites for substituting them with laser active ions such as neodymium ($\text{Nd}^{3+}$) (Yi Lu and Guofu Wang 2003a), erbium ($\text{Er}^{3+}$) (Yi Lu et al 2003b), and ytterbium ($\text{Yb}^{3+}$) (Aron et al 2001) as their ionic radii are similar and further they exists in the trivalent state. In the present work, $\text{Nd}^{3+}$ was added to LCOB in order to make it a laser-host crystal.

The melting point of the RECOB crystals decreases with the increase in the ionic radius of the rare earth ion present in it (Hiroshi Nakao et al 2006). Since the radius of the lanthanum ion ($\text{La}^{3+}$) is large among the rare
earth ions, the lanthanum calcium oxy borate (LCOB) crystal has the lowest melting point of 1410 °C.

The successful growth of pure LCOB and Nd$_x$La$_{(1-x)}$COB (x=0.2) single crystals from the melt was carried out in the present investigation. The thermal cycles opted for the growth of both the crystals were maintained the same and the growth was carried out. The characterization studies were performed on pure and Nd$_{0.2}$La$_{0.8}$COB single crystals and the results are analyzed. A brief introduction on the neodymium ion and the crystal growth set up employed for the growth of LCOB and NdLCOB crystals are presented.

5.1.1 Neodymium ions (Nd$^{3+}$)

Neodymium (Nd) is a chemical element belonging to the group of rare earth metals. In laser technology, it is widely used in the form of trivalent ions (Nd$^{3+}$) as the laser-active dopant of gain media based on various host materials, including both crystals and glasses. Various neodymium doped crystals include, Nd:Y$_3$Al$_5$O$_{12}$ (Nd:YAG) (Krennrich et al 2008a, 2008b, Geusic et al 1964), Nd:YVO$_4$ (neodymium doped yttrium vanadate) (Fornasiero et al 1998), Nd:YLiF$_4$ (Nd:YLF, neodymium doped yttrium lithium fluoride) (Santo et al 2006), Nd:GDD (neodymium doped gadolinium gallium garnet), Nd:YAlO$_3$ (Massey 1972), Nd$^{3+}$:LaF$_3$ (Waynant et al 1985) (neodymium doped lanthanum fluoride).

The energy level diagram of Nd$^{3+}$ ion is shown in Figure 5.1. The usual pump wavelength is 808 nm (for Nd:YAG; wavelengths for other host materials may differ), but a higher slope efficiency can be achieved by directly pumping into the upper laser level $^4F_{3/2}$ with 869 nm light. The strongest laser transition is that from $^4F_{3/2}$ to $^4I_{11/2}$ for 1064 nm, but other transitions are available with longer or shorter wavelengths. In order to
achieve lasing on those, lasing at the 1064 nm line needs to be suppressed by inserting an appropriate wavelength filter (usually consisting of one or more dichroic mirrors) into the cavity. Via multi-phonon emission, the populations in levels $^4I_{11/2}$ to $^4I_{15/2}$ are quickly transferred to the ground-state manifold $^4I_{9/2}$. Hence, there is normally negligible population in all these levels, so that neodymium-doped gain media exhibit pure four-level behavior. The exception is the case where the lower level is the ground-state manifold $^4I_{9/2}$: 946-nm Nd:YAG lasers (and other Nd-based lasers emitting between 900 and 1000 nm) are quasi-three-level lasers, exhibiting a fairly high threshold pump power.

![Energy level structure of the trivalent neodymium ion](image)

**Figure 5.1 Energy level structure of the trivalent neodymium ion**

Except for glasses, in all the gain media, the neodymium dopant ions replace other ions (often yttrium) of the host medium, which have about the same size.
5.1.2 Crystal Growth Setup

Single crystal growth of LCOB crystals are conventionally carried out by employing radio frequency (RF) furnaces. But for the first time, growth of LCOB and NdLCOB single crystals were carried out by employing resistive furnaces. Single crystal growth of LCOB and NdLCOB crystals were carried out from their melts. Hence, a resistive heating furnace made of molybdenum-di-silicide (MoSi$_2$) heating elements were designed and fabricated. The furnace is shown in Figure 5.2. To avoid the breakdown of the heating rods at high temperatures, we had replaced the U-shaped MoSi$_2$ rods with rods with 90° between the hot and cold zones. This had helped in the successful operation of the rods over a long period. The design of the inner chamber of the high temperature furnace is shown in the Figure 5.3. R-type thermocouples were used as temperature sensors. High quality alumina bricks were employed for thermal insulation. The furnace employed in the present work was controlled using Eurotherm 2604 model single loop controller which has the precision of ± 0.1 °C.

5.2 MATERIALS SYNTHESIS

The starting materials for the growth of LCOB and NdLCOB crystals were prepared by following the chemical reactions (5.1) and (5.2) respectively.

\[
\text{La}_2\text{O}_3 + 8\text{CaCO}_3 + 3\text{B}_2\text{O}_3 \rightarrow 2\text{LaCa}_4\text{O(BO}_3\text{)_3} + 8\text{CO}_2 \uparrow \quad (5.1)
\]

\[
(0.8)\text{La}_2\text{O}_3 + (0.2)\text{Nd}_2\text{O}_3 + 8\text{CaCO}_3 + 3\text{B}_2\text{O}_3 \rightarrow 2\text{La}_{0.8}\text{Nd}_{0.2}\text{Ca}_4\text{O(BO}_3\text{)_3} + 8\text{CO}_2 \uparrow \quad (5.2)
\]
Figure 5.2 High temperature furnace constructed using molybdenum di silicide heating elements
Both the reactions were carried out separately in platinum crucibles. The rare earth oxides, calcium carbonate and boron-tri-oxide of more than 4N purity were heated to 1100 °C for 24 hours for decomposing the calcium carbonate. Calcium oxide (CaO) can be used directly instead of calcium carbonate, but since calcium oxide is highly hygroscopic, calcium carbonate was employed. The obtained product was again well-mixed and ground. It was again heated to 1200 °C in a platinum crucible for 24 hours. The synthesized LCOB and NdLCOB polycrystalline materials are formed only in the second step. The obtained polycrystalline LCOB and NdLCOB materials were confirmed through powder XRD analysis. The powder X-ray diffraction pattern of LCOB and NdLCOB materials are shown in Figures 5.4 (a) and 5.4(b).
5.3 SINGLE CRYSTAL GROWTH

The melting point of pure LCOB material is reported to be around 1410 °C (Daniel Vivien et al 2002). Since, the ratio of Nd:La in NdLCOB material was only 1:4, the melting point of NdLCOB must also be nearer to 1410 °C. Hence, the polycrystalline materials of LCOB and NdLCOB were taken in platinum crucibles separately and were heated to a temperature of 40 °C above the melting point of LCOB. The melt was maintained at that temperature for 24 hours to homogenize the melt and to expel the bubbles out of the melt.
The inner growth chamber of the furnace was viewable only till the temperature of 1300 °C, but above the temperature of 1400 °C, wherein the polycrystalline materials actually melt, the growth chamber cannot be viewed easily and hence seeded growth could not be attempted. The inner growth chamber of the high temperature furnace at 1300 °C and 1400 °C are shown in Figures 5.5 (a) and 5.5 (b) respectively. After melting the material and homogenization, slow cooling was performed and the cooling rates were varied between 0.5 - 60 °C/hr. The thermal cycle adopted for the growth of LCOB and NdLCOB single crystals was maintained the same and is shown below.

\[
\text{Room temperature} \rightarrow @ 60^\circ \text{C/hr.} \rightarrow 1450^\circ \text{C} \rightarrow @ 24 \text{ hrs.} \rightarrow 1450^\circ \text{C} \rightarrow @ 1^\circ \text{C/hr.} \rightarrow 1425^\circ \text{C} \\
\rightarrow @ 0.5^\circ \text{C/hr.} \rightarrow 1385^\circ \text{C} \rightarrow @ 5^\circ \text{C/hr.} \rightarrow 1200^\circ \text{C} \rightarrow @ 60^\circ \text{C/hr.} \rightarrow \text{Room temperature.}
\]

Transparent single crystals of LCOB and NdLCOB with the dimensions of 15 x 9 x 5 mm\(^3\) and 5 x 5 x 3 mm\(^3\) respectively were obtained. The obtained LCOB and Nd: LCOB single crystals are shown in Figures 5.6 (a) and 5.6 (b) respectively.

![Figure 5.5 Growth chambers at (a) 1300 °C (b) 1400 °C](image)
Figure 5.6 (a) LCOB crystals (b) NdLCOB crystals
5.4 CHARACTERISATION

The grown crystals were subjected to various characterisation studies such as powder XRD, single crystal XRD, HRXRD analysis, UV-VIS-NIR, FTIR analysis, dielectric measurements, powder SHG test, photoluminescence studies, specific heat studies and laser damage threshold (LDT) measurements. The results are discussed.

5.4.1 Powder X-ray Diffraction Analysis

The powder XRD spectra recorded for the LCOB and NdLCOB single crystals are shown in Figure 5.2 (c) and 5.2 (d) respectively. On comparing the two powder XRD patterns, it is evident that the LCOB and NdLCOB crystals are iso-structural in nature.

5.4.2 Single Crystal XRD Analysis

The single crystal XRD data recorded for the LCOB and NdLCOB single crystals also reveals the fact that, there is no considerable effect of Nd$^{3+}$ ions in altering the unit cell parameters of LCOB. The single crystal XRD data of the LCOB crystal is found to be in accordance with the available reports (Zhang et al 2004). The results of the single crystal XRD measurements are summarized in Table 5.1. The single crystal XRD data for the Nd$_x$La$_{1-x}$COB single crystal (with $x$=0.2) is not available in literature.
Table 5.1 Single crystal XRD data

<table>
<thead>
<tr>
<th>Parameters</th>
<th>LCOB crystal</th>
<th>NdLCOB crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As-grown</td>
<td>Reported value</td>
</tr>
<tr>
<td>Unit cell parameters</td>
<td>a= 8.14 Å</td>
<td>a= 8.16 Å</td>
</tr>
<tr>
<td></td>
<td>b=16.01 Å</td>
<td>b=16.08 Å</td>
</tr>
<tr>
<td></td>
<td>c=3.60 Å</td>
<td>c=3.63 Å</td>
</tr>
<tr>
<td>Bond angle</td>
<td>α=γ= 90°</td>
<td>α=γ= 90°</td>
</tr>
<tr>
<td></td>
<td>β = 101.23°</td>
<td>β = 101.3°</td>
</tr>
<tr>
<td>Crystal system</td>
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<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C_m</td>
<td>C_m</td>
</tr>
</tbody>
</table>

5.4.3 HRXRD Analysis

The multicrystal X-ray diffractometer shown in the Figure 3.4 was used for the present investigation. The well-collimated and monochromated MoKα₁ beam obtained from the three monochromator Si crystals set in dispersive (+,−,−) configuration has been used as the exploring X-ray beam. The specimen crystals (LCOB and NdLCOB separately) is aligned in the (+,−,−,+) configuration. The diffraction curve (DC) was recorded by the ω scan mode wherein the detector was kept at the same angular position 2θB with wide opening for its slit. For both the specimens, before recording the diffraction curve, to remove the surface of the crystal and also to ensure surface planarity, the specimens were first lapped and chemically etched in a non-preferential etchant. The diffraction curves recorded on the LCOB and NdLCOB crystals are shown in Figures 5.7 (a) and 5.7 (b). The DC for both the crystals was recorded for similar planes and the FWHM values were found to be very lesser which is an indication of good crystalline quality. The FWHM for LCOB crystal is 38 arc s and that for NdLCOB crystal is 34 arc s.
Figure 5.7  Diffraction curve recorded for (a) LCOB crystal (b) NdLCOB crystal
5.4.4 UV-VIS-NIR Analysis

The UV-VIS-NIR spectral transmittance was recorded with the single crystals of LCOB and NdLCOB with 2 mm thicknesses in the wavelength range of 200-1100 nm. The recorded transmission spectra of LCOB and NdLCOB single crystals are shown in Figure 5.8 (a) and 5.8 (b) respectively. The lower cutoff wavelength for both the crystals is at 210 nm. The LCOB single crystal is nearly 80% transparent and NdLCOB single crystal is about 75% transparent in the UV and visible regions. The lower cutoff value (210 nm) of the crystals is in good agreement with the available reports. The absorption peaks at 355, 535, 585, 590, 742, 810, 815 and 875 nm in the spectrum recorded for the NdLCOB crystal are due to the inter sub band transitions of the Nd$^{3+}$ ions (Yi Lu et al 2003a, Mougel et al 1997). The radiative transitions recorded for NdLCOB crystal are summarized in Table 5.2. The wide transmission in the UV and visible regions enables the materials to be used for the higher order harmonics of Nd: YAG laser sources. Further, when pumped with a wavelength which is absorbed by a NdLCOB crystal, the crystal can be used as a laser material.

5.4.5 Energy Dispersive X-ray Analysis (EDAX)

The EDAX measurement was carried out on the NdLCOB crystal to identify the presence of Nd in the crystal. The measurement was performed using a Hitachi SEM instrument. The observed EDAX spectrum is shown in Figure 5.9. The presence of both La and Nd are evident from the spectrum.
Figure 5.8  UV-VIS-NIR spectrum of (a) LCOB crystal (b) NdLCOB crystal

Table 5.2 Radiative transitions observed in NdLCOB crystal

<table>
<thead>
<tr>
<th>Transitions ($^4I_{9/2} \rightarrow$)</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4D_{1/2}, ^4D_{5/2}, ^4D_{3/2}$</td>
<td>355</td>
</tr>
<tr>
<td>$^4G_{9/2}$</td>
<td>535</td>
</tr>
<tr>
<td>$^4G_{5/2}$</td>
<td>585</td>
</tr>
<tr>
<td>$^4G_{7/2}$</td>
<td>595</td>
</tr>
<tr>
<td>$^4F_{7/2},^4S_{3/2}$</td>
<td>742</td>
</tr>
<tr>
<td>$^2H_{9/2}$</td>
<td>810</td>
</tr>
<tr>
<td>$^4F_{5/2}$</td>
<td>815</td>
</tr>
<tr>
<td>$^4F_{3/2}$</td>
<td>875</td>
</tr>
</tbody>
</table>
5.4.6 FTIR Analysis

The FTIR spectrum was recorded using the KBr pellet method in the wavenumber ranging from 450 – 4000 cm\(^{-1}\) for the LCOB and NdLCOB crystals. The spectra are shown in the Figures 5.10 (a) and 5.10 (b) for LCOB and NdLCOB crystals respectively. The present investigation is in good agreement with the results obtained for other borates indicating the wavenumbers of fundamental vibrations of \((\text{BO}_3)^3^-\) ions in the three distinct regions 1350-1200, 790-730 and 680-590 cm\(^{-1}\). The absorption peaks around 1230 cm\(^{-1}\) in both the figures are due to the asymmetric stretching modes of \((\text{BO}_3)^3^-\) ions. The absorption peaks around 750 cm\(^{-1}\) and 615 cm\(^{-1}\) for both the crystals are due to the symmetric and the asymmetric bending modes of \((\text{BO}_3)^3^-\) ions. The absorption peaks near 515 cm\(^{-1}\) is due to the internal vibration of Ca-O bond. The vibration due to the lanthanum and the oxygen atom (La-O) is indicated by the peaks near 450 cm\(^{-1}\). The vibration due to the neodymium and oxygen atoms occurs usually below 100 cm\(^{-1}\) which is out of the measuring range of the instrument. The FTIR spectrums for both the crystals are quite similar and all the possible peaks of the LCOB and NdLCOB crystals are present in the FTIR spectrum.

![Figure 5.9 EDAX spectrum of NdLCOB crystal](image-url)
Figure 5.10  FTIR spectrum of (a) LCOB and (b) NdLCOB crystal
5.4.7 Dielectric Studies

Nonlinear polarization of the crystals with respect to the applied electric field causes the phenomena of nonlinear optics to arise. The polarization of the crystals with respect to the applied electric field forms the base for dielectric measurements. Hence, in order to study the dielectric behaviour of the crystals, LCOB and NdLCOB crystals were subjected to dielectric studies. Transparent polished crystals with a thickness of 4 mm were used for the studies. 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 50 Hz to 5 MHz. The dielectric constant was calculated using the relation (5.3)

\[
\varepsilon_r = \frac{Cd}{\varepsilon_0 A}
\]

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 5.11 (a) and 5.11 (b) show the variation of dielectric constant and loss for different frequencies of LCOB and NdLCOB single crystals at room temperature. The dielectric constant and dielectric loss curves for LCOB and NdLCOB crystals are similar. From the curves it is evident that the dielectric constant and dielectric loss decreases slowly with the increasing frequencies and attains saturation at higher frequencies. The low dielectric value of the crystal at high frequency can be attributed to the space charge polarization. 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.
Figure 5.11 (a) Dielectric constant, (b) Dielectric loss measurements
5.4.8 Powder SHG Test

The second harmonic generation (SHG) efficiency of the grown LCOB and NdLCOB crystals was measured using the powder technique of Kurtz and Perry. The second harmonic output was generated by irradiating powder samples using a pulsed laser beam of a Nd:YAG laser as discussed in section 2.5.7. The output power of LCOB sample was 440 mV, and for KDP was 145 mV. The output power of NdLCOB sample was 515 mV, and for KDP was 155 mV. The powder SHG efficiency of LCOB and NdLCOB crystals were found to be 3 and 3.3 times that of KDP which was used as the reference material.

5.4.9 Photoluminescence (PL) Studies

The photoluminescence studies were performed on the NdLCOB crystal. The emission spectrum is shown in Figure 5.12. The infrared emission at 1064 nm was observed for the crystal excited with 355 nm radiation. The FWHM of the emission peak is much lesser than 0.5 nm, which indicates the emission of a highly coherent beam. The emission corresponds to the \( ^4F_{3/2} \rightarrow ^4I_{11/2} \) transition of the \( \text{Nd}^{3+} \) ions.

![Emission spectrum recorded for the NdLCOB crystal](image)

Figure 5.12 Emission spectrum recorded for the NdLCOB crystal
5.4.10 Specific Heat Measurements

Specific heat is one of the important factors that influence the damage threshold of a crystal (Xu et al 1997). Till now, there no reports available in literature, on the dependence of specific heat of the NdLCOB crystal on temperature. The specific heat measurement was recorded for the NdLCOB single crystal using a Perkin Elmer DSC-7 model instrument. The measurements were carried out in nitrogen atmosphere. 35 mg of the sample was taken. The sample was heated at the rate of 20 °C/min. The recorded spectrum is shown in Figure 5.13. The specific heat value of the NdLCOB crystal is 0.17235 J/g°C at 55 °C and is 0.97593 J/g°C at 550 °C respectively. The result indicates that the NdLCOB crystal must have a high laser damage threshold value.

Figure 5.13 Dependence of specific heat of NdLCOB crystal on Temperature
5.4.11 Laser Damage Threshold Studies

The LCOB and NdLCOB single crystals are non-hygrosopic materials possessing higher transmission down to the ultraviolet region (210 nm). The LCOB and NdLCOB crystals can be employed as NLO and as laser crystals respectively. To find the adaptability of these crystals for laser applications involving higher temperatures, the laser damage threshold studies were performed. As discussed in the section 2.5.6, a Q-switched Nd:YAG laser for 20 ns laser pulses at the wavelength of 1064 nm was employed. The pulse repetition rate was 10 Hz. Laser damage threshold value of the LCOB and NdLCOB crystals were determined to be 2.206 and 2.209 GW/cm² respectively. As inferred from the specific heat measurements, the NdLCOB crystal has appreciable thermal behavior with higher LDT value.

5.5 CONCLUSIONS

The growth of LCOB and NdLCOB single crystals were carried out by melt technique by opting similar thermal cycle and growth conditions. The grown crystals were subjected to characterization studies such as X-ray diffraction studies, UV-VIS-NIR studies, FTIR, dielectric, powder SHG test, PL studies, specific heat measurements and laser damage tolerance studies. The iso-structural nature of both the crystals is confirmed and there is only a very small deviation observed in the single crystal XRD data.

The cutoff wavelength for both LCOB and NdLCOB single crystals occur at 210 nm. But, there are various absorption peaks in the visible region for and the NdLCOB crystal which are mainly due to the inter sub-band transitions of the Nd³⁺ ions. The NdLCOB crystals can be used as laser host materials by pumping them with a laser wavelength which is absorbed by the Nd³⁺ ion.
The possible functional groups of the LCOB and the NdLCOB single crystals are observed in the FTIR analysis. The dielectric loss for both the crystals is very low and hence they are highly suitable for device applications. The powder SHG efficiency of the crystals is also high when compared to KDP crystal and hence it can act as an efficient nonlinear optical crystal. The NdLCOB crystal was pumped at 355 nm laser radiation and the infrared emission at 1064 nm was successfully demonstrated.

The specific heat measurement was carried out for the NdLCOB crystal to find its adaptability in devices involving high temperatures. The specific heat values recorded are observed to be good. The laser induced damage studies were carried out for LCOB and NdLCOB crystals which reveals that both the crystals have damage tolerances in the GW/cm² range. The results suggest that the LCOB single crystal is an excellent NLO crystal and NdLCOB single crystal can act as both an NLO and also as a good laser crystal.