CHAPTER 2

GROWTH AND CHARACTERISATION OF YTTRIUM CALCIUM OXY BORATE (YCOB) SINGLE CRYSTALS FROM LITHIUM CARBONATE FLUX

2.1 INTRODUCTION

The discovery of laser has initiated significant advancements in science and technology. Immediately after the creation of the first laser in 1960, interactions between light and materials have been widely investigated. Franken and his co-workers were the first to observe radiation with double the frequency of a ruby laser when it was passed through a quartz crystal (Franken et al 1961). This was the first observation of second harmonic generation (SHG).

The monochromatic and coherent laser radiations are widely employed in applications including optical communication systems, data storage discs, medical diagnostics and so on. Because of their very high photon energies and the ability to be highly focused, radiations with shorter wavelengths are preferred. For instance, photon energy in the UV region is sufficient to induce bond breaking process in many materials. High power UV lasers are available from rare-gas halide excimer lasers - eg. XeCl, ArF, KrF (William Silfvast 2003). However, the excimer lasers involve the usage of corrosive gases, have bulkier dimensions and pose several complexities in
usage. A compact, maintenance-free, solid-state alternative is therefore which can replace the excimer lasers were desired.

Because of the intrinsically short upper laser lifetime of the UV laser active media and the requirement of intensive electron pumping to the excitation state, direct lasing from solid-state medium is highly challenging. An effective technique for the UV generation is cascaded sum frequency generation pumped by the output of near IR ($\lambda$~1 µm) solid state lasers by using nonlinear optical (NLO) crystals. For instance, the fundamental wavelength ($\lambda = 1064$ nm) of a Nd:YAG laser can be converted to second ($2\omega$, $\lambda=532$ nm), third ($3\omega$, $\lambda=355$ nm), fourth ($4\omega$, $\lambda=266$ nm), fifth harmonic generations ($5\omega$, $\lambda=213$ nm) nm respectively. Hence, in the recent times, there is an increasing number of investigations involving the crystal growth and systematic study of several nonlinear optical materials that can be employed for the generation of UV radiations.

Several inorganic borate based single crystals are efficient NLO materials that have gained importance in the recent years. Yttrium calcium oxy borate (YCOB) crystals belong to the RECOB family of crystals. These crystals have proved to be excellent NLO materials for the harmonic generations of Nd:YAG lasers. YCOB single crystals were conventionally grown using the melt techniques such as Bridgman technique or the Czochralski technique. Yiting Fei and his coworkers have grown YCOB crystals with the dimensions of 3 inch in diameter and 7 inch in length using Iridium crucible by Czochralski technique (Yiting Fei et al 2006). Kuzmicheva and his research group have studied the structure of Czochralski method grown Ce, Er, Yb:YCOB crystal (Kuzmicheva et al 2002). The influence of dopants on the damage threshold property of the YCOB crystal grown by the Czochralski technique was analyzed by Brahadeeswaran and his coworkers (Srinivasan Brahadeeswaran et al 2005). YCOB crystals were
grown from Bridgman technique by Jun Luo and his team and reported (Jun Luo et al 2001).

In the present investigation, the growth of YCOB single crystals by the flux technique were performed for the first time using two different fluxes – lithium carbonate (Li$_2$CO$_3$) and boron-tri-oxide (B$_2$O$_3$). This chapter discusses the successful growth of YCOB single crystals from lithium carbonate flux and the characterization studies performed on the grown crystals.

### 2.2 PROPERTIES OF YTTRIUM CALCIUM OXY BORATE (YCOB)

Yttrium calcium oxy borate single crystals have the chemical formula YCa$_4$O(BO$_3$)$_3$. It crystallizes with the monoclinic crystal structure with the space group C$_m$ (Li et al 2000). There are two kinds of isolated (BO$_3$)$^{3-}$ groups present in the crystal. They lie in planes perpendicular to [001] for one group and are skewed by ~30° for the other. There are also two types of distorted octahedral Ca$^{2+}$ sites and Y$^{3+}$ ions are located in the mirror plane of the monoclinic structure, in six-fold coordination with C$_s$ site symmetry (Krishnakumar and Nagalakshmi 2004). The crystal structure is shown in Figure 2.1. YCOB melts congruently at 1510 °C (Makoto Iwai et al 1997, Klimm et al 2003). YCOB crystals are grown by the conventional Czochralski (Cz) technique using iridium (Ir) crucibles in argon (Ar) atmosphere. YCOB crystal possesses good mechanical stability and is non-hygroscopic which makes them fit for device applications.

Though the lattice parameters of GdCOB and YCOB crystals are similar, but since the YCOB crystal has relatively larger birefringence of 0.041 at $\lambda$=1064 nm, it allows them to generate UV lasers from them, by
generating the third harmonic generation (THG) of a Nd:YAG laser source (1064 nm + 532 nm → 355 nm) which is not possible in GdCOB crystals. A few properties of the YCOB single crystals are enlisted in the Table 2.1.

The phase-matching angles for THG in type-1 YCOB crystal are (θ,φ) = (90°, 73.2°) and (58.7°, 90°) in the xy- and yz-planes. The effective NLO coefficient of YCOB for THG is higher along (θ,φ) = (90°, 73.2°) in the xy-plane and was estimated to be 0.52 pm/V which is 1.4 times larger than that of KDP (type-2, d_{eff}=0.3507 pm/V) (Eimerl 1987).

Figure 2.1 Crystal structure of YCOB
Table 2.1 Selected properties of YCOB crystals

<table>
<thead>
<tr>
<th>Properties</th>
<th>YCOB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$C_m$</td>
</tr>
<tr>
<td>Unit cell parameters</td>
<td>$a=8.04\text{ Å}$</td>
</tr>
<tr>
<td></td>
<td>$b=15.95\text{ Å}$</td>
</tr>
<tr>
<td></td>
<td>$c=3.51\text{ Å}$</td>
</tr>
<tr>
<td>Bond angle</td>
<td>$\alpha=\gamma=90^\circ$</td>
</tr>
<tr>
<td></td>
<td>$\beta = 101.19^\circ$</td>
</tr>
<tr>
<td>Hygroscopicity</td>
<td>Non-hygroscopic</td>
</tr>
<tr>
<td>Transparency range</td>
<td>220 - 3600 nm</td>
</tr>
<tr>
<td>Melting point</td>
<td>1510 °C</td>
</tr>
<tr>
<td>Hardness</td>
<td>6.5 mhos</td>
</tr>
<tr>
<td>Mechanical properties</td>
<td>Good</td>
</tr>
<tr>
<td>Effective nonlinear coefficient</td>
<td>1.1 pm/V</td>
</tr>
<tr>
<td>Density</td>
<td>3.2 g/cm$^3$</td>
</tr>
</tbody>
</table>

2.3 SYNTHESIS OF POLYCRYSTALLINE YCOB MATERIALS

The starting material was prepared according to the following reaction shown in equation (2.1).

$$\text{Y}_2\text{O}_3 + 8\text{CaCO}_3 + 3\text{B}_2\text{O}_3 \rightarrow 2\text{YCa}_4\text{O} (\text{BO}_3)_3 + 8\text{CO}_2 \uparrow$$  (2.1)

Reactants of 3N purity and above were used to synthesize the polycrystalline YCOB material. The synthesis of the polycrystalline materials was carried out in two steps (Kawamura et al 2002). The reactants were well-mixed and ground and were calcined at 1100 °C in a platinum crucible for 24
hours. This step was performed to eliminate the absorbed water present in the material and to decompose the carbonate present in the mixture. After cooling to room temperature, the obtained product was again well-mixed and ground and was heated to 1200 °C in a platinum crucible for 24 hours. The obtained product was the polycrystalline YCOB material which was confirmed through powder XRD analysis. The powder XRD pattern of the YCOB polycrystalline material is shown in Figure 2.2 (a).

Figure 2.2  Powder XRD pattern of (a) Synthesized YCOB material (b) YCOB single crystal
2.4 SINGLE CRYSTAL GROWTH

The synthesized charge along with the lithium carbonate flux was taken at different weight proportions and the differential thermal analysis (DTA) was performed to identify the charge – to - flux ratio which would favour the crystal growth of YCOB. Lithium carbonate decomposes on melting and hence lithium oxide (Li$_2$O) acts as the flux. However, since lithium oxide is very hygroscopic, it cannot be used as the flux directly. The differential thermal analysis was performed using a NETZSCH - Gerateban GmbH thermal analysis instrument. Alumina was employed as the reference material. The thermal analysis of the samples was done with a heating rate of 10 K/min.

The synthesized polycrystalline YCOB powder was taken along with lithium carbonate flux in the following weight proportions – YCOB: Li$_2$CO$_3$ = 1:0.3, 1:0.4, 1:0.5 and 1:0.6. Differential thermal analysis was carried out on all the samples. The DTA pattern obtained is shown in Figure 2.3.

The melting of Li$_2$CO$_3$ occurs at 676.3 °C in all the combinations. Further, lithium carbonate decomposed on melting at 676.3 °C as per the following reaction expressed in equation (2.2),

\[
\text{Li}_2\text{CO}_3 \rightarrow \text{Li}_2\text{O} + \text{CO}_2 \uparrow 
\]

Lithium oxide (Li$_2$O) alone acts as the flux. The melting of YCOB polycrystalline powder occurs only in the 1:0.4 and 1:0.5 ratios at 910°C and at 873.2°C respectively as shown in Figure 2.3. There are no observations with regard to the melting of YCOB powder in 1:0.3 and 1:0.6 ratios. Since,
there is a near congruent peak at 910 °C in the 1:0.4 selection, crystal growth was preferred and attempted with this combination.

![Figure 2.3 DTA pattern of YCOB with flux in different weight proportions (YCOB:flux = a. 1:0.3, b. 1:0.4, c. 1:0.5, d. 1:0.6)](image)

The synthesized polycrystalline YCOB material along with the flux was taken in the ratio 1:0.4 in a platinum crucible and the following thermal cycle was adopted for the growth of YCOB single crystals.

Room temperature \(\rightarrow\) 60°C/hr. \(\rightarrow\) 975°C \(\rightarrow\) 24 hrs. \(\rightarrow\) 975°C \(\rightarrow\) 1°C/hr. \(\rightarrow\) 875°C \(\rightarrow\) 2°C/hr. \(\rightarrow\) 700°C \(\rightarrow\) 5°C/hr. \(\rightarrow\) 500°C \(\rightarrow\) 50°C/hr. \(\rightarrow\) Room temperature

Several transparent single crystals of size 3 x 3 x 5 mm\(^3\) were successfully harvested from the corners of the crucible. The grown YCOB crystals were harvested manually from the edges of the crucible. Since, the flux employed had solidified at the centre of the crucible; removal of the
crystals from the flux was not complicated. Figure 2.4 shows the photograph of the as-grown crystals obtained.

2.5 CHARACTERIZATION

Characterization studies are important for the assessment of the quality of the grown crystals and to find its properties. X-ray diffraction technique is widely used for studying crystalline materials to assess their structural properties (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 it’s structural, optical, elemental, surface and NLO properties. It is highly essential to know all these properties of a crystal to employ it for device applications.

Figure 2.4 YCOB crystals grown from lithium carbonate flux
2.5.1 X-ray Diffraction Analysis

The X-ray diffraction data of the YCOB single crystal was collected using Enraf - Nonius CAD - 4 diffractometer, with graphite monochromated CuK$_\alpha$ radiation source. The powder of the grown YCOB crystals were analyzed by powder X-ray diffraction studies using a Rich Seifert diffractometer with CuK$_\alpha$ ($\lambda=1.540$ Å) radiation at a scan rate of 0.5 °/min. The X-ray studies were carried out at room temperature. The powder XRD pattern confirmed the formation of YCOB single phase. The powder XRD pattern of the grown YCOB crystal is shown in Figure 2(b).

Single crystal XRD studies reveal that YCOB crystal belongs to the monoclinic system, the space group is C$_{m}$ and the cell parameters are $a=8.043$ Å, $b=15.953$ Å, $c=3.512$ Å, $\alpha=\gamma=90^\circ$ and $\beta=101.2^\circ$. The obtained cell parameters are in good agreement with the earlier reports (Makoto Iwai et al 1997).

2.5.2 UV-VIS-NIR Analysis

Transmission spectra are of much importance for NLO materials, since an NLO material can be used in optical devices only if it has a wide transparency range. To find the transmission range of YCOB crystals, the UV-VIS-NIR spectral transmittance was recorded with an as-grown single crystal of YCOB with 2 mm thickness in the wavelength range of 200-1100 nm. Shimadzu UV-1061 spectrophotometer was employed to record the spectrum. The recorded transmission spectrum is shown in Figure 2.5. The lower cutoff wavelength for the YCOB crystal was around 220 nm. The as-grown crystal was nearly 55% transparent in the UV and visible regions. The lower cutoff value obtained for the flux-grown YCOB crystal is in good
agreement with the YCOB crystals grown using the Czochralski method (Petra Becker 1998). The presence of a wide transmission in the UV and visible regions enables sufficient transmission of the higher order harmonics of Nd: YAG lasers.

Figure 2.5 UV-VIS-NIR spectrum of YCOB crystal

Figure 2.6 EDAX spectrum obtained for the YCOB crystal
2.5.3 EDAX Studies

Energy dispersive analysis by X-rays (EDAX) analysis is a powerful tool in determining the presence of elements in a given sample. The EDAX spectrum of the YCOB crystal was obtained using an INCA 200 energy dispersive X-ray microanalyser. The EDAX spectrum obtained in the study is shown in Figure 2.6. The presence of the constituent elements of the YCOB crystal was confirmed by the occurrence of their respective peaks. There were no signs for the presence of lithium in the crystal. Hence, the growth of ‘flux inclusion-free’ crystal has been confirmed.

2.5.4 FTIR Analysis

FTIR analysis was carried out to confirm the presence of functional groups and their vibration modes in the YCOB crystals. The sample to be studied was prepared by mixing it with potassium bromide (KBr) powder and a pellet was prepared. The FTIR spectrum was recorded in the range 4000 – 400 cm\(^{-1}\). The spectrum is shown in Figure 2.7. 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 four distinct regions 1350-1200, 950-930, 790-730 and 680-590 cm\(^{-1}\) (Maczka et al 2004). The absorption peaks at 1207.19 cm\(^{-1}\) and 937.06 cm\(^{-1}\) are due to the asymmetric and the symmetric stretching modes of \((\text{BO}_3)^{3-}\) ions. The absorption peaks at 746.26 cm\(^{-1}\) and 615.87 cm\(^{-1}\) are due to the symmetric and the asymmetric bending modes of \((\text{BO}_3)^{3-}\) ions. The absorption peak at 514.30 cm\(^{-1}\) is due to the internal vibration of Ca-O bond. The vibration due to the yttrium and the oxygen atom which is not bonded with the \((\text{BO}_3)^{3-}\) ion is indicated by the peak at 451.89 cm\(^{-1}\). Hence, all the possible peaks of the YCOB crystal are present in the FTIR spectrum.
Etching studies were carried out to understand the growth mechanism and to assess the perfection of the grown crystals. Etching is the selective dissolution of the crystal, which is used to reveal the lattice defects (Sangwal 1987). To analyze the surface morphology, an as-grown transparent crystal was selected for the observation of etch patterns. The crystal was selected and 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 using dilute nitric acid as the etchant at room temperature. The etching duration was 5 minutes. ‘Hillock-like’ patterns were observed as shown in Figure 2.8.
Figure 2.8 Optical micrograph of the etched YCOB crystal

Figure 2.9 LDT measurement setup
2.5.6 Laser Induced Damage Threshold (LDT) Measurement

The laser induced damage threshold (LDT) is an important parameter for any crystal to be used in laser applications. The grown crystal can be used in conjunction with high power lasers only if it has a high LDT value. On irradiating a crystal with high power lasers, 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 LDT value differs with respect to the wavelength, pulse width, repetition rate of the incident beam for the same crystal itself.

In the present investigation, laser damage threshold value of yttrium calcium oxy borate (YCOB) 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 was 10 Hz. The experimental setup used for the laser damage studies is shown in Figure 2.9.

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 lens with a focal length of 20.5 cm is used, which determines the spot size on the sample. 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 YCOB crystal was found to be 2.4 GW/cm$^2$. The result indicates that the grown YCOB single crystals can be opted for high power laser applications.

### 2.5.7 Powder SHG Measurement

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 YCOB single crystals by using the Kurtz powder technique (Kurtz and Perry 1968). Pulse energy of 3.6 mJ/pulse with the pulse width of 8 ns and repetition rate of 10 Hz was used. 90° geometry was employed. The fundamental beam was filtered by using a monochromator. The Photo multiplier tube (Philips Photonics) was used as the detector. The setup used for the measurement is shown in Figures 2.10 and Figure 2.11. It is observed that the measured SHG efficiency of YCOB crystals was twice that of standard KDP which was employed as the reference material. The raw data is also presented.

![Schematic of the apparatus used in the Kurtz powder SHG measurement](image-url)
2.6 CONCLUSIONS

Polycrystalline samples of YCOB were synthesized by the method of solid state reaction. The synthesized polycrystalline material was confirmed by powder X-ray diffraction studies.

Thermal analysis was performed with polycrystalline YCOB powder and lithium carbonate flux in different weight proportions to identify the optimum charge-to-flux ratio that would favour the growth of YCOB crystals. Single crystals of YCOB were grown using the flux technique for the first time by the method of slow-cooling. The grown crystals were confirmed by powder X-ray diffraction studies. The lattice parameters and the crystal structure were confirmed by single crystal X-ray diffraction studies.

The optical characteristics of the YCOB crystals were examined using a UV-VIS-NIR spectrophotometer which clearly revealed the transmission of nearly 55% in the UV, visible and near IR regions. The formation of ‘flux inclusion-free’ crystals was confirmed by the EDAX measurements. The presence of the functional groups of the YCOB crystals was confirmed by FTIR measurements. The etching studies were carried out which reveals the presence of ‘hillock-like’ etch pits in the surface of the crystal.

The powder SHG test was carried out for the YCOB crystals and the YCOB crystal has the SHG efficiency twice that of KDP. The laser damage threshold value of the YCOB crystal was found to be 2.4 GW/cm².

These results demonstrate that flux technique is a promising method for the growth of YCOB crystals. The characteristics of the grown
crystals have been compared with those of the crystals grown by the conventional melt techniques. The flux technique has eliminated the problems faced in the conventional melt techniques such as – the necessity to maintain inert atmosphere, complex crystal growth arrangements and viewing problems. Hence, it can be concluded that flux technique is a more promising technique to grow YCOB crystals.