CHAPTER 3

GROWTH OF YTTRIUM CALCIUM OXY BORATE SINGLE CRYSTALS FROM B₂O₃ FLUX

3.1 INTRODUCTION

As reported in Chapter 2, the YCOB single crystals were grown from lithium carbonate flux for the first time. Though, the growth temperature was reduced, there were serious problems encountered during the growth of YCOB crystals from lithium carbonate flux, as listed below.

a. The formation of a gel layer prevented the viewing of crystal growth.

b. The optical quality of the grown crystals was poor.

c. The size of the grown crystals was very lesser and could not be improved.

These problems paved way for looking into a new flux, which can overcome these difficulties and can yield better results. Lead oxide (PbO) and bismuth oxide (Bi₂O₃) were used separately as flux with YCOB and DTA was recorded. Both the fluxes did not dissolve YCOB and finally, boron-tri-oxide (B₂O₃) was chosen as the flux. Boron tri oxide is advantageous over lithium carbonate as the flux, since boron tri oxide serves as self-flux and it can also act as an ‘encapsulant’ (Bystrova et al 2005) during the single crystal growth of YCOB.
3.1.1 Properties of Boron tri Oxide

The following properties of boron tri oxide have made it a versatile flux for the growth of several oxide crystals such as lithium niobate, lithium borate, barium borate and etc. A few properties of boron tri oxide are listed below.

a. The melting point of boron tri oxide is 450 °C, which is very lesser than the melting point of the material to be grown.

b. Boron tri oxide acts as an ‘encapsulant’ which prevents the evaporation of the liquid during growth.

c. Boron tri oxide flux can be separated both from crystal and the crucible by constantly boiling it in water or in weaker acids, hence post-growth cleaning is easier.

3.1.2 Crystals Grown using Boron Tri Oxide Flux

A variety of single crystals belonging to semiconductors, oxide crystals and etc are grown from boron tri oxide flux for various applications. Boron tri oxide alone is used in some cases, whereas in many other cases boron oxide is used along with other fluxes such as lead oxide, lead fluoride, calcium oxide and etc. the selection of either boron oxide alone or the combination of boron oxide flux with other solvents depends on the crystals to be grown and are unique for the crystals of interest. Neodymium doped yttrium aluminium garnet (Nd:YAG) (Jerry Hobb 1994), lithium niobate (Marshall et al 2007), sapphire (Al₂O₃), yttrium iron garnet (YIG) (Robert Heimann and Wolfgang Tolksdorf 1983, Van Erk 1979), titanium oxide (TiO₂), yttrium chromium oxide (YCrO₃), borate crystals such as cesium lithium borate (CLBO) (Xin Yuan et al 2006), barium borate (BBO) (Fedorov
et al 2008), lanthanum calcium borate (LCB) (Fangli Jing et al 2005) are examples of crystals that are grown from boron tri oxide fluxes.

3.2 SINGLE CRYSTAL GROWTH

Polycrystalline YCOB materials were prepared by the method of solid state reaction as discussed in the section 2.3. The single crystal growth of YCOB crystals from boron tri oxide flux was attempted as per the following procedure.

The polycrystalline YCOB powder was taken along with the boron-tri-oxide flux in the ratio of 1:2 (YCOB:B$_2$O$_3$) in a platinum crucible. The melting point of the YCOB material is reported to be around 1510 °C (Klimm et al 2002, Leonyuk et al 2003). But the YCOB polycrystalline powder is found to dissolve in the boron-tri-oxide flux in the temperature range of 1000-1030 °C. Hence the thermal cycle was designed accordingly.

The optimized thermal cycle employed for the growth of YCOB single crystals is as follows.

Room temperature → @ 60°C/hr. → 1030 °C → @ 24 hrs. → 1030 °C → @ 1°C/hr. → 975 °C
→ @ 3°C/hr. → 800 °C → @ 5°C/hr. → 600 °C → @ 50°C/hr. → Room temperature.

The graphical representation of the thermal cycle opted is shown in Figure 3.1. The slope of the curve corresponds to the rate of heating/cooling. Several transparent YCOB single crystals with the dimensions 5 x 5 x 10 mm$^3$ were obtained. The separation of the crystals from the flux was simpler. This was achieved by constantly boiling the crucible in water for about 1 week. The grown YCOB crystals are shown in Figure 3.2.
Figure 3.1 Graphical representation of the thermal cycle

Figure 3.2 As-grown YCOB crystals
3.3 CHARACTERIZATION

The grown YCOB crystals were characterized by various studies. The structural properties were studied by powder XRD and single crystal XRD analyses. The structural perfection was assessed by high resolution X-ray diffraction studies. The optical transmission studies were carried out using UV-VIS-NIR studies and the functional groups were analysed by fourier transform infrared (FTIR) spectroscopy. The nonlinear optical property of the YCOB crystals was determined using the Kurtz Perry technique. The laser induced damage tolerance of the YCOB crystals was determined to find the suitability of the crystal in high power devices. The results are analyzed and discussed in detail.

3.3.1 Powder X-ray Diffraction Study

The powder of the YCOB crystal was analyzed by the powder X-ray diffraction studies using a Rich Seifert diffractometer with CuKα radiation source (λ = 1.540 Å) at a scan rate of 0.05 °/min. The X-ray studies were carried out at room temperature. The obtained powder XRD pattern is shown in Figure 3.3. The powder XRD pattern matches well with the previously available reports (Huaidong Jiang et al 2002). There are no occurrences of peaks other than the peaks corresponding to the YCOB compound. Hence, the formation of YCOB single phase is confirmed.
3.3.2 Single Crystal X-ray Diffraction Study

The X-ray diffraction data of the YCOB single crystal was collected using a Enraf-Nonius CAD - 4 diffractometer, with graphite monochromated CuK$_\alpha$ radiation source. Single crystal X-ray diffraction studies reveal that YCOB crystal belongs to the monoclinic system. The space group is C$_{m}$ and the cell parameters are $a = 8.0$ Å, $b = 15.9$ Å, $c = 3.5$ Å, $\alpha = \gamma = 90^\circ$ and $\beta = 101.2^\circ$. The obtained cell parameters are similar to the values available for the YCOB crystal in earlier reports (Makoto Iwai et al 1997).

3.3.3 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
YCOB single crystal. Figure 3.4 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 MoK\(\alpha_1\) and MoK\(\alpha_2\) components. The MoK\(\alpha_1\) beam is isolated with the help of fine slit arrangement and allowed to further diffract 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 MoK\(\alpha_1\) beam away from the Bragg diffraction peak and thereby gives a good collimated and monochromatic MoK\(\alpha_1\) 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 (YCOB 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 YCOB 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 curve recorded on the (111) plane of YCOB crystal is shown in Figure 3.5. The full width at half maximum (FWHM) of the diffraction curves is 23 arc s, which reveals that the crystalline quality of the grown crystal is good.
3.3.4 UV-VIS-NIR Studies

The YCOB crystal is grown for employing it in optical devices. Hence, in order to find the transmission range of the YCOB crystals and to find whether the usage of flux had altered the cutoff wavelength of the crystal, the UV-VIS-NIR spectral transmittance was recorded for an YCOB single crystal with 2 mm thickness in the wavelength range of 190-1100 nm. The recorded transmission spectrum is shown in Figure 3.6. The lower cutoff wavelength for the YCOB crystal was around 220 nm. The as-grown crystal is nearly 78% transparent in the UV and visible regions. The lower cutoff value is in accordance with the YCOB crystals grown using the Czochralski method (Furuya et al 1999). The presence of a wide transmission in the UV and visible regions enables sufficient transmission of the higher order harmonics of Nd:YAG laser sources.
Figure 3.6 UV-VIS-NIR spectrum of YCOB crystal

Figure 3.7 FTIR spectrum of YCOB crystal
3.3.5 Fourier Transform Infrared (FTIR) Analysis

The FTIR spectrum was recorded for the YCOB crystal using the KBr pellet method. The spectrum is shown in Figure 3.7. The fundamental vibrations of (BO$_3$)$_3^-$ ions are observed in the four distinct regions 1350-1200, 950-930, 790-730 and 680-590 cm$^{-1}$. The absorption peaks at 1207.19 cm$^{-1}$ and 937.06 cm$^{-1}$ are due to the asymmetric and the symmetric stretching modes of (BO$_3$)$_3^-$ ions. The absorption peaks at 746.26 cm$^{-1}$ and 615.87 cm$^{-1}$ are due to the symmetric and asymmetric bending modes of (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 oxygen atom which is not bonded with (BO$_3$)$_3^-$ ions is indicated by the peak at 451.89 cm$^{-1}$. All the functional groups that are characteristic of the YCOB crystal are present in the FTIR spectrum.

3.3.6 Powder SHG Measurement

The fundamental beam with the wavelength of 1064 nm from a Q switched Nd:YAG laser was used to test the Second Harmonic Generation (SHG) property of the grown YCOB single crystals by using the Kurtz powder technique. The setup used for the measurement is shown in Figure 2.10. It is observed that the measured SHG efficiency of YCOB crystals was twice that of standard KDP which was employed as the reference material.

3.3.7 Laser Damage Threshold Study

The YCOB crystal is a non-hygroscopic material possessing higher transmission down to the ultraviolet region (220 nm). Hence, the crystal can be used in a variety of applications in conjunction with high power lasers. In order to check, whether the flux grown crystal has high LDT value or not, 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 YCOB crystal was found to be 2.4 GW/cm². There is no change in the laser damage threshold value of the YCOB crystal grown from lithium carbonate or boron tri oxide fluxes.

3.4 CONCLUSIONS

Polycrystalline YCOB powder was synthesized by the solid-state reaction method. The materials were confirmed by powder X-ray diffraction studies. The growth of YCOB single crystals from the boron-tri-oxide flux was carried out for the first time. The growth temperature was identified to be in the range of 1000-1030 °C.

Since the boron oxide rich solution was highly viscous, growth by pulling was not feasible. Hence, YCOB single crystals were grown from boron tri oxide flux by slow cooling method. YCOB single crystals with the dimensions of 5 x 5 x 10 mm³ were harvested from the crucible. Though seeded growth could not be attempted when boron tri oxide flux was used, but the problems such as ‘gel layer’ formation, growth of crystals with poor optical quality and the non-feasibility to grow bulk crystals, which were encountered during the growth of YCOB crystals from lithium carbonate flux could be avoided.

The grown YCOB crystals were subjected to various characterization studies. The formation of YCOB single phase was confirmed by powder XRD analysis. The lattice parameters of the YCOB crystals were calculated from the single crystal XRD analysis. High resolution X-ray diffraction studies performed on the grown crystals reveals that the crystalline perfection of the YCOB crystals was good. The YCOB crystal is highly
transparent in the visible and UV regions. The cutoff wavelength of the YCOB crystal is 220 nm. This makes the crystal more suitable for device applications involving UV lasers. The FTIR analysis confirms the presence of all the functional groups in the grown YCOB single crystal. The bond assignments corresponding to the functional groups were made. The SHG efficiency of the YCOB crystal was calculated using the Kurtz Perry technique. The powder SHG efficiency of the YCOB crystal was found to be twice that of KDP. The laser induced damage threshold value of YCOB crystal was determined to be 2.4 GW/cm$^2$.

The results obtained indicate that the flux technique is a best alternate method to melt technique for the growth of YCOB single crystals with high optical quality. Among lithium carbonate and boron tri oxide fluxes, boron tri oxide is highly advantageous to grow bulk YCOB crystals with improved optical quality.