CHAPTER 1

A REVIEW ON BORATE-BASED CRYSTALS

1.1 INTRODUCTION

Crystals have attracted mankind in the past owing to their aesthetic appearance. But the scientific and technological aspects and applications of crystals are understood only in the present century. In particular, with the advent of transistors in the early half of twentieth century, crystals became inevitable to any further developments in modern technology (Laudise 1970). Moreover, crystal growth which had existed previously as a small area in the field of materials science now enjoys a unique status and its progress is unavoidable for the benefit of mankind. The impact of single crystals in the field of solid state lasers and other optical devices has led to tremendous technological advancements. The search for new potential materials – their structural design and engineering, materials synthesis, single crystal growth has become the thrust area in materials research.

Recent developments in the field of nonlinear optics hold promise for important applications in optical information processing, telecommunication and integrated optics. Electro-optic, nonlinear optical and photorefractive materials are active media which can be used in a variety of devices in which light waves have to be manipulated by electrical and optical fields.
A laser beam consists of a number of beneficial characteristics such as, good coherence, high density, high-speed responsivity, diverse wavelength and frequency (Bosshard et al 1995). These characteristics are highly essential to realize high-speed, large capacity information transmission and storage. In order to utilize the various optical functions of a laser beam completely, the second or third order nonlinear optical response of a material for an electric field at optical frequency is employed. In particular, the development of electrically and optically controlled devices such as frequency converters, electro-optic modulators or photorefractive nonlinear devices employing the second-order nonlinear optical response, including the first-order electro-optic effect, is actively taking place.

The requirements for an excellent nonlinear optical (NLO) crystal include high nonlinear coefficient, moderate birefringence, higher transparency in the wavelength of interest and several other desirable parameters (Takatomo Sasaki et al 2000). There are several reports on the growth and characterization of NLO crystals available in literature. They are mainly categorized as organic, inorganic and semi-organic NLO crystals.

The organic NLO crystals have the advantage in possessing high nonlinear optical coefficient. But the main drawback with the organic crystals is that their thermal and mechanical stabilities are too low that their usage with high power lasers is hindered. Various efficient organic crystals include POM (Boomadevi et al 2004a), L-PCA (Boomadevi and Dhanasekaran 2004b), etc.

Semi-organic NLO crystals involve the combination of a metal with an organic ligand. The metal complexes offer variety of structures, higher environmental stability and a much greater diversity of tunable opto-
electronic properties (Nalwa 1991). Allyl thiourea cadmium chloride (ATCC) (Sun et al 2003), bis-glycine sodium nitrate (BGSN) (Sankar et al 2007) are some examples of semi-organic crystals which are employed in devices.

But the chemical bonding and the mechanical properties of inorganic crystals are superior over organic and semi-organic crystals and hence are reliable materials. Inorganic NLO crystals are versatile candidates for device applications. Their mechanical strength and thermal withstanding capabilities make them to be employed in devices in conjunction with high power laser sources. There are various inorganic NLO crystals available such as, KTiO(PO$_4$) (KTP) (Dongxiang Zhang et al 2008), KH$_2$PO$_4$ (KDP) (Kun Li and Binzhang 2008), periodically poled LiNbO$_3$ (PPLN) (Ravi Bhushan et al 2008), etc.

1.2 CRYSTAL GROWTH

For the crystal growth of any material, a supersaturated mother phase is the primary requirement. The initial stage of crystallization in this supersaturated system is the formation of nuclei of the crystalline phase. By the process of crystal growth, these nuclei attain macroscopic dimensions. In general, the crystallization process occurs by the three steps,

i. Achievement of supersaturation or supercooling,
ii. Formation of crystal nuclei and
iii. Single crystal growth.

1.2.1 Crystal Growth Techniques

Various crystal growth techniques have been developed over the years to meet the needs for basic scientific and technological applications.
The crystal growth methods are mainly classified according to the nature of phase transitions involved in growing them as follows:

(i) Solid-Solid phase transformation: Solid growth

(ii) Liquid-Solid phase transformation: Solution growth, Melt growth

(iii) Vapour-Solid phase transformation: Vapour growth

The choice of selecting a particular crystal growth technique depends on the physical and chemical properties of the material to be crystallized and the suitability of the technique to grow the desired crystal. The parameters such as the growth kinetics, size, shape, purity, quality and the cost involved in producing the crystals also play a vital role (Pamplin 1980). The growth of borate based crystals from the melt technique and by the high temperature solution growth method was adopted in the present work and hence an overview of these techniques along with a brief discussion on the crystal growth systems employed is summarized.

1.2.1.1 High Temperature Solution Growth (or) Flux Technique

Crystal growth techniques can be classified into two categories:

i. Growth from a single component system

ii. Growth from poly component systems.

In a single component system, only the chemical constituent to be crystallized is present in the growth system. In the poly component systems, another chemical component (flux) is also added along with the chemical to be crystallized. The primary reason for the addition is to lower the
crystallization temperature. This reduction in the growth temperature is highly essential if the material to be crystallized has an incongruently melting behavior or it has higher vapor pressures at high temperatures (Elwell and Scheel 1975).

The second component usually taken acts as the solvent, that will dissolve the material to be crystallized (i.e. solute) at high temperatures. The properties of an ideal solvent include,

i. Higher solubility

ii. The required crystal phase must be the only stable phase

iii. Appreciable change in solubility with temperature

iv. Low viscosity, in the range of 1 to 10 centipoise is preferred

v. Low melting point

vi. Lower volatility at the maximum working temperature

vii. Lesser reactivity with the crucible

viii. High pure chemical with lower cost in higher quantities is preferred.

In general, the above enlisted properties cannot be realized in any fluxes used in real time applications. But a compromise is often arrived, depending on the type of the crystals to be grown, their size, technique adopted for growth and so on. The common chemicals that are widely used as fluxes are potassium fluoride (KF) (Koichi Watanabe and Fumiyoshi Taguchi 1993), sodium fluoride (NaF) (Lijuan Liu and Chuangtian Chen 2006), boron tri oxide (B₂O₃), lead fluoride (PbF₂) and their mixtures. In the present
investigation, growth of YCOB single crystals were performed with lithium carbonate ($\text{Li}_2\text{CO}_3$) and boron tri oxide ($\text{B}_2\text{O}_3$) fluxes.

### 1.2.1.2 Melt Technique

Nearly 85% of the crystals that are used in various applications are being grown from the melt techniques of crystal growth. Czochralski technique, Bridgman-Stockbarger technique, Kyropoulos technique, zone melting technique, Verneuil technique are some of the widely used methods to grow crystals from melt. In the present investigation, growth of LCOB and Nd:LCOB crystals were carried out by slowly cooling their respective melts, as the seeded growth cannot be performed at very high temperatures (above 1400 °C) which needs very high sophistication. Growth of YCB single crystals were attempted both by slow cooling and also by pulling methods. The preferable properties of materials that can be grown by melt techniques are,

i. The material must melt congruently

ii. The material should possess relatively low vapor pressures

iii. The desired phase of the material to be crystallized must be possible

iv. There should not be any reaction between the crucible and the chemicals at higher operating temperatures.

A variety of oxide materials, semiconductors, halides, etc. are grown from melt techniques.
1.3 NONLINEAR OPTICS

1.3.1 Introduction

The successful demonstration of lasers by Maiman and his co-workers in the year 1960 paved way for various scientific and technological advancements in the twentieth century (Maiman 1960). A new field – Nonlinear optics came into being. Franken and his co-workers were the first to realize the nonlinear optical effect when they observed light at twice the frequency of a ruby laser ($\lambda=693.4$ nm) from a quartz crystal which was subjected to the ruby laser radiation. The practical observation of nonlinear optical phenomena would not have been observed if the lasers were not invented. This can be explained as follows. The field strengths of the conventional light sources used prior to the advent of lasers was of the order of $10^3$ V/m. But the interatomic field strengths lie in the range between $10^7$ and $10^{10}$ V/m. Hence, the conventional light sources are very less intense to affect the atomic fields to the extent of altering the optical parameters associated with it. The unique property of lasers – its coherence, helped in achieving radiations with the intensities of the order of $10^{10}$ V/m feasible. Hence, lasers serve as useful and essential tool for the field of nonlinear optics and other related interesting phenomena such as Kerr effect, Pockels effect, second or higher harmonic generations and so on.

The origin of NLO processes is the response of a nonlinear dielectric medium to an oscillating electric field. For example, when a dielectric material is subjected to an electromagnetic (e.m) radiation, the propagation of the e.m wave through the material produces changes in the spatial and temporal distribution of electric charges due to the interaction between the e.m wave, electrons and atoms. This perturbation creates electric dipoles whose manifestation is macroscopic polarization ($P$). When the
applied electric field (E) is very small, the induced polarization can be expressed as equation (1.1),

$$P = \varepsilon_0 \chi^{(1)} E$$  

(1.1)

where $\varepsilon_0$ is the permittivity of free space ($\varepsilon_0 = 8.854 \times 10^{-12}$ C$^2$/kg m$^3$) and $\chi^{(1)}$ is the linear susceptibility term which is responsible for the optical properties such as absorption, index of refraction, dispersion and birefringence of the medium. When the applied electric field is highly intense and comparable to the inter-atomic field, the induced polarization is given by equation (1.2),

$$P = \varepsilon_0 (\chi^{(1)} E + \chi^{(2)} E.E + \chi^{(3)} E.E.E + ... )$$  

(1.2)

where $\chi^{(2)}, \chi^{(3)}$ are the second and the third order nonlinear susceptibilities and their magnitude decreases as their order increases ($\chi^{(1)} : \chi^{(2)} : \chi^{(3)} = 1:10^{-8}:10^{-16}$). The second order susceptibility term ($\chi^{(2)}$) gives rise to second harmonic generation, frequency mixing and parametric generation and the third order susceptibility term ($\chi^{(3)}$) is responsible for the third harmonic generation, Stimulated Raman scattering, optical bistability and phase conjugation.

### 1.3.2 Desired Properties of NLO Crystals

For the purpose of reliable laser frequency conversion, NLO crystals with the following properties are desired.

i. Large NLO coefficient

ii. Moderate birefringence

iii. Small walk-off effect
iv. Large angular, spectral and temperature bandwidths
v. Wide transparency in the wavelength of interest
vi. High laser induced damage threshold
vii. Ease of growth
viii. Low material cost
ix. Good chemical stability
x. Good mechanical stability

Till 1975, extensive research on NLO crystals based on the P-O, I-O and Nb-O bonds were carried out. The widely studied NLO crystals include KDP (KH₂PO₄), LN (LiNbO₃), LiIO₃ and etc as they fulfill the above listed requirements to a good extent. With the advent of potassium penta borate (KB₅O₈.4H₂O) crystal in the year 1975, tremendous attention was directed to grow borate based crystals for frequency conversion purposes.

1.4 NLO BORATE CRYSTALS

The large family of borate compounds is a suitable chemical playground now adopted by many materials scientists, because the extremely wide variability of borate crystal chemistry allows the creation of various different structure types (Xue et al 2000). Furthermore, among all the borate structures reported till date, 36% are non-centrosymmetric while among the reported inorganic crystal structures there are in total only 15% of non-centrosymmetric structure (Aka and Brenier 2003).

Borate crystals are superior in UV applications to other commonly used NLO materials such as potassium di hydrogen phosphate (KDP) or lithium niobate (LN) because of their high transmittance at wavelengths down
to 155 nm combined with higher damage threshold. A comparison of selected NLO materials is given in the Table 1.1. The first borate crystal described for UV light generation was potassium penta borate (KB$_5$O$_8$.4H$_2$O) (Dewey et al 1975). However, intense research work on borate crystals was initiated only after the development of β-BaB$_2$O$_4$ (BBO) and LiB$_3$O$_5$ (LBO).

**Table 1.1 Comparison of damage threshold and optical transmittance range of selected NLO materials**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Damage threshold at λ=1064 nm and $\tau_p$=10 ns (GW/cm$^2$)</th>
<th>Optical transmittance range (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KH$_2$PO$_4$</td>
<td>~ 0.25</td>
<td>174-1570</td>
</tr>
<tr>
<td>LiNbO$_3$</td>
<td>0.3</td>
<td>400-5500</td>
</tr>
<tr>
<td>LiIO$_3$</td>
<td>0.12</td>
<td>280-6000</td>
</tr>
<tr>
<td>KTiOPO$_4$</td>
<td>1.0</td>
<td>350-4500</td>
</tr>
<tr>
<td>LiB$_3$O$_5$</td>
<td>&gt; 0.9</td>
<td>155-3200</td>
</tr>
<tr>
<td>β-BaB$_2$O$_4$</td>
<td>5</td>
<td>189-3500</td>
</tr>
<tr>
<td>Li$_2$B$_4$O$_7$</td>
<td>~ 40</td>
<td>170-3500</td>
</tr>
</tbody>
</table>

The optical properties of borate crystals can be related to their molecular structure. A few borate crystals are mentioned in the Table 1.2 as examples. These crystals are constructed from the three basic structure units: (B$_3$O$_6$)$_3^-$, (B$_3$O$_7$)$_5^-$ and (BO$_3$)$_3^-$ anionic groups. The (B$_3$O$_6$)$_3^-$, (B$_3$O$_7$)$_5^-$ and (BO$_3$)$_3^-$ anionic groups are shown in Figure 1.1. 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).
Due to the planar hexagonal structure of the \((\text{B}_3\text{O}_6)^{3-}\) anionic group, borate crystals constructed from this basic unit have greater \(\chi^{(2)}\) compared to crystals composed of \((\text{B}_3\text{O}_7)^{5-}\) and \((\text{BO}_3)^{3-}\) anionic groups. Thus in terms of NLO coefficients, the \((\text{B}_3\text{O}_6)^{3-}\) group is the most suitable as the basic structure unit of NLO borate crystals followed by \((\text{B}_3\text{O}_7)^{5-}\) group and then \((\text{BO}_3)^{3-}\) group. However, the UV absorption edge of the borate crystals constructed from the \((\text{B}_3\text{O}_6)^{3-}\) group occurred at a longer wavelength (e.g. BBO) when compared to those constructed from \((\text{B}_3\text{O}_7)^{5-}\) group (e.g. LBO, CBO, CLBO). Calculations showed that \(\pi\)-conjugated orbitals of planar \((\text{B}_3\text{O}_6)^{3-}\) tend to shift the UV absorption edge to toward the red. As one of the boron atoms in \((\text{B}_3\text{O}_6)^{3-}\) changed from trigonal to tetrahedral coordination, thereby forming nonplanar \((\text{B}_3\text{O}_7)^{5-}\) groups, the \(\pi\)-conjugated orbital system is weakened, as in the case of LBO and CBO and the UV absorption edge shifts to 160-170 nm. Both CBO and LBO are constructed from a continuous network of non-planar \((\text{B}_3\text{O}_7)^{5-}\) groups with interstitial cesium and lithium cations, respectively. Based on the absorption edge, therefore, \((\text{B}_3\text{O}_7)^{5-}\) group is ideal as the basic structural unit of deep UV NLO materials. Likewise, if the dangling bonds of the three terminated oxygen atoms of \((\text{BO}_3)^{3-}\) groups are interlinked with cations, an absorption edge appearing at wavelengths as short as 155 nm is also feasible as in the cases with KBBF and SBBO.
Figure 1.1 Basic structure units of (a) BO₃ (b) B₃O₆ (c) B₃O₇ borates
(Dark circles represent boron and bright circles represent oxygen atoms)
Table 1.2 Selected properties of some NLO borate crystals

<table>
<thead>
<tr>
<th>Crystals</th>
<th>Space group</th>
<th>Transparency range (nm)</th>
<th>Nonlinear coefficient (pm/V)</th>
<th>Birefringence Δn</th>
<th>Basic structure unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-BaB₂O₄ (BBO)</td>
<td>R 3c</td>
<td>190 - 3300</td>
<td>d₁₁ = 1.844</td>
<td>0.12 at 1064 nm</td>
<td>B₃O₆</td>
</tr>
<tr>
<td>LiB₃O₅ (LBO)</td>
<td>Pnn 2₁</td>
<td>160 - 2600</td>
<td>d₃₁ = 0.94, d₃₂ = 1.13, d₃₃ = 0.256</td>
<td>0.04 at 1064 nm</td>
<td>B₃O₇</td>
</tr>
<tr>
<td>CsB₃O₅ (CBO)</td>
<td>P2₁2₁2₁</td>
<td>167 – 3400</td>
<td>d₁₄ = 0.863</td>
<td>0.053 at 1064 nm</td>
<td>B₃O₇</td>
</tr>
<tr>
<td>KBe₂BO₃F₂ (KBBF)</td>
<td>R 32</td>
<td>155 – 3660</td>
<td>d₁₁ = 0.8</td>
<td>~0.072 at 589 nm</td>
<td>BO₃</td>
</tr>
<tr>
<td>Sr₂Be₂BO₇ (SBBO)</td>
<td>P 6₃</td>
<td>155 – 3780</td>
<td>d₁₅ = 2</td>
<td>~0.062 at 589 nm</td>
<td>BO₃</td>
</tr>
<tr>
<td>CsLiB₆O₁₀ (CLBO)</td>
<td>142 d</td>
<td>180 - 2750</td>
<td>d₃₆ = 0.95</td>
<td>0.050 at 1064 nm</td>
<td>B₃O₇</td>
</tr>
<tr>
<td>YCa₄O(BO₃)₃ (YCOB)</td>
<td>Cₙ</td>
<td>220 - 3600</td>
<td>d=1.1</td>
<td>0.041 at 1064 nm</td>
<td>BO₃</td>
</tr>
</tbody>
</table>

Borate that are not only employed for frequency conversion but also as self-frequency doubling (SFD) active laser sources are being developed in the recent years. Mainly borate crystals belonging to the huntite type are chosen for self-frequency doubling applications. The families of borate crystals with the general chemical formula, RAl₃(BO₃)₄ with R=Y, Nd, Sm, Eu, Tb, Dy, Er and RX₃(BO₃)₄ with R=Gd, Sm, X=Cr, Al are grown and
studied. The emissions of sharp bright lines from these crystals were observed. These crystals are chemically stable, non-hygroscopic and have high hardness. These crystals melt incongruently and are grown from flux methods only. All these crystals are trigonal with the space group R32. The widely studied huntite-type borate crystal is $\text{YAl}_3(\text{BO}_3)_4$ (YAB) (Ali Reshak et al 2008). These crystals are doped with Er, Nd and Yb ions for making them as SFD crystals. It is commonly grown by top seeded solution growth (TSSG) method.

YAB is a non-centrosymmetric crystal and as early as in 1974 it was reported as a very effective second-harmonic generating material. Furthermore, owing to its good chemical stability and the possibility of substituting $\text{Y}^{3+}$ ions with other lanthanide ions, namely $\text{Nd}^{3+}$, $\text{Yb}^{3+}$, and $\text{Er}^{3+}$, it is a good material for laser applications. The nonlinear optical properties of this material along with lasing properties led to the fabrication of numerous systems generating red, green and blue lights due to self-frequency doubling effect (Jaque et al 1999). They also possess relatively large two-photon absorption. These compounds are promising candidate as second and third order optical materials (Majchrowski et al 2005). At the same time they are good matrices for different rare-earth ions (Dominiak-Dzik et al 2004, You et al 2004). Reports are also available on the $\text{Nd}^{3+}$, $\text{Tb}^{3+}$, $\text{Yb}^{3+}$, and $\text{Er}^{3+}$ doped YAB crystals (Jaque et al 1998, Jing Li et al 2004a, Jing Li et al 2004b).

Further, in the family of borate crystals with huntite structure, research on crystals such as $\text{NdAl}_3(\text{BO}_3)_4$ (NAB), $\text{ErAl}_3(\text{BO}_3)_4$ (ErAB), $\text{YbAl}_3(\text{BO}_3)_4$ (YbAB) is carried out in the present years (Leonyuk et al 2007). The melting points of these materials are below 1300 °C. These crystals are grown by flux techniques and are mainly employed in SFD purposes.
Though there is a tremendous amount of work on BBO and LBO crystals, due to the reason that they are grown from flux melts which yields crystals with lesser dimensions, research on borate crystals exhibiting congruently melting behavior has gained interest. Borate based NLO crystals with congruently melting nature are mainly grown from Czochralski technique. CsLiB$_5$O$_{10}$ (CLBO) crystals, which are the structural derivatives of LBO crystals, are grown in larger dimensions from their melts. Very large CLBO single crystals with the dimensions of $140 \times 110 \times 110$ mm$^3$ with good optical quality were grown and reported.

Another derivative of LBO is CsB$_3$O$_5$ (CBO) compound also melts congruently. Its melting point is 842 °C. Crystals with dimensions of 20 mm in diameter and 30 mm in length were grown with the pulling rate of 8 mm/day.

Isostructural borate crystals of SrB$_4$O$_7$ and PbB$_4$O$_7$, both of which belong to the orthorhombic crystal system are grown from their melts. Large single crystals of PbB$_4$O$_7$ were grown by the Czochralski technique from a melt with a slight excess of PbO to lower the viscosity of the melt at 774 °C. Seed crystals with the [100] or [001] orientations were preferred for single crystal growth. Growth runs, with a cooling rate of 0.7 °C/day and a pulling rate of 4 mm/day has yielded single crystals with $20 \times 28 \times 55$ mm$^3$ dimensions. In the similar manner, single crystals of SrB$_4$O$_7$ were grown from its stoichiometric melt at 994 °C. Single crystals with 25 mm diameter and 20 mm length were grown using pulling rates of 2 mm/day with the crystal rotation of 20 rpm.

Intense research on the incongruently melting borate crystals is also in progress. Due to the fact that a few incongruently melting borate materials
are transparent down to vacuum UV region, single crystal growth of these materials is undertaken.

The family $\text{MBe}_2\text{BO}_3\text{F}_2$, with $\text{M}=$Na, K is an example of a structure type with isolated $[\text{BO}_3]$ triangles, crystallizing in the non-centrosymmetric space group R32. The potassium compound $\text{KBe}_2\text{BO}_3\text{F}_2$ (KBBF) was first synthesized in the year 1968. These crystals were grown from flux melts with KBF$_4$ and BeO. The plate-like crystals with the dimensions of 10 x 10 x 0.3 mm$^3$ were reported.

Improvement of the NLO properties by enhancing the number of NLO active $[\text{BO}_3]$ groups per unit volume of the crystal structure was attempted by creating $\text{Sr}_2\text{Be}_2\text{B}_2\text{O}_7$ (SBBO). These crystals exhibit the hexagonal crystal system and were grown by the TSSG technique. These crystals are grown by slow cooling with the cooling rate of 1-2 °C/day. Crystals with the dimensions of 7 x 7 x 3 mm$^3$ with good optical quality are obtained and reported.

In general, a good NLO crystal that can generate deep UV light effectively is required to have a birefringence between that of BBO ($\Delta n=0.12$ at $\lambda=1064$ nm) and LBO ($\Delta n=0.04$ at $\lambda=1064$ nm). This allows the expansion of the phase matching range for SHG at a reasonably low walk-off effect and significantly large phase-matching bandwidths. The earlier mentioned CLBO crystal, has $\Delta n=0.052$ at $\lambda=1064$ nm and hence it is widely used for deep-UV light conversion. Thus several NLO crystals like CLBO that possess a birefringence between that of BBO and CLBO are desired. SBBO ($\Delta n=0.062$ at $\lambda=589$ nm) and KBBF crystals ($\Delta n=0.072$ at $\lambda=589$ nm) are attractive candidates in this aspect. However, because of the weak binding between the layered structural units, KBBF is difficult to grow and is mechanically fragile.
(Chen et al 1995). The SBBO has strong covalent bonds between beryllium atoms and oxygen atoms in adjacent layers. This makes SBBO mechanically stronger and relatively easy to grow compared to KBBF. However, beryllium is toxic, which makes crystal growth inconvenient. Thus, it is important that the Be atoms in SBBO be replaced by a nontoxic element. Sasaki and his coworkers had attempted to replace the \((\text{BeO}_4)^{6-}\) with \((\text{AlO}_4)^{5-}\) and had replaced \(\text{Sr}^{2+}\) with \(\text{M}^{+}\) \((\text{M}^{+} = \text{Li}^{+}, \text{Na}^{+}, \text{K}^{+}, \text{Rb}^{+} \text{and Cs}^{+})\) according to the concept of ionic compensation \((\text{Al}^{3+} + \text{K}^{+} \rightarrow \text{Be}^{2+} + \text{Sr}^{2+})\). In this way, potassium aluminum borate crystal with the chemical formula \(\text{K}_2\text{Al}_2\text{B}_2\text{O}_7\) (KAB) was discovered. KAB has the spatial arrangement similar to that of SBBO.

The structure of the KAB crystal is trigonal with the P321 space group. The lattice parameters of the crystal are \(a=b=8.5657 \, \text{Å}, c=8.463 \, \text{Å}, V=537.7 \, \text{Å}^3\) and \(Z=3\) (Hu et al 1998). The KAB crystals are grown from flux technique. Different fluxes such as \(\text{B}_2\text{O}_3\), \(\text{K}_2\text{CO}_3\), \(\text{K}_2\text{CO}_3\cdot\text{B}_2\text{O}_3\), alkali halides such as \(\text{KF}\) and \(\text{NaF}\) were used for the growth of KAB crystals and are reported. The KAB crystal is transparent from 180-3600 nm. The thermal property of the KAB crystal is also studied. The linear thermal expansion coefficient of the KAB crystal along the \(x\), \(y\) and \(z\) directions are very lesser. The specific heat values of KAB crystal at 47.6 °C and 294.6 °C are 1.0084 J/g °C and 1.39 J/g °C (Chengqian Zhang et al 2003).

1.5 CRYSTALS CHOSEN FOR THE PRESENT INVESTIGATION

1.5.1 Rare earth calcium oxy borate (RECOB)

The first member of the rare earth calcium oxy borate (RECOB) crystals with the chemical composition of \(\text{RECa}_4\text{O}(\text{BO}_3)_3\) \((\text{RE}=\text{Sm})\) was synthesized by Khamaganova and his co-workers in the year 1991.
(Khamaganova et al 1991). Later intense work on the growth and characterization of this family of crystals with various rare earth elements such as La, Nd, Gd, Er, Y were carried out and reported. The RECOB family of crystals appears to be attractive candidates for NLO applications as they possess the non-centrosymmetric structure which is an essential parameter for any NLO material. Widely studied RECOB crystals include YCOB, GdCOB and LCOB crystals. The RECOB crystals with the rare earth ions with electronic configurations $4f^n$, $n\neq 0,7,14$ give rise to electronic transitions in the visible region that would interfere with the expected NLO properties.

The RECOB crystals melt congruently and were conventionally grown by the Czochralski and Bridgman techniques of crystal growth. The melting temperatures of the RECOB crystals increases with a decrease in the ionic radii of the rare earth ion present in it (Hiroshi Nakao et al 2006). Accordingly, the melting points of LCOB, GdCOB and YCOB single crystals are 1410, 1480 and 1510 °C respectively (Daniel Vivien et al 2002).

The RECOB single crystals exhibit the monoclinic crystal structure with the $C_m$ space group. They are biaxial crystals. These crystals offer the advantage in providing suitable sites for doping them with ‘laser-active’ ions, since the widely used ‘laser-active’ ions such as neodymium, erbium, ytterbium have similar ionic radii and occur in the trivalent state as that of the rare earth ion present in the RECOB crystals (Mougel et al 1997, Lupei et al 2002).

### 1.5.2 Yttrium Calcium Borate (YCB)

Another emerging borate-based crystal family is rare earth calcium borate (RCB) crystals, with the general chemical formula $R_2CaB_{10}O_{19}$ ($R$ represents rare earth element). In this series of crystals, only crystal growth
of pure and doped lanthanum calcium borate (LCB) are performed and reported in literature. There are no reports available on any other materials in the RCB family of crystals. The LCB crystal is reported to be insensitive to moisture, has high hardness (6.5 mhos) and is transparent from 180 nm to 3300 nm. Moreover, the laser damage threshold (LDT) value of the LCB crystal is also very high (11.5 GW/cm² for 1064 nm, 8 ns radiation) (Fangli Jing et al 2008). Various reports on ‘laser-active’ ion doped LCB crystals are also available in literature (Guo et al 2005a). Crystal growth of yttrium calcium borate (YCB) single crystals are attempted for the first time. The single crystal growth of YCB and the characterization studies performed on the grown crystals are also discussed.

1.6 SCOPE OF THE PRESENT INVESTIGATION

The main objectives of the present investigations are categorized as follows.

i. To synthesize polycrystalline materials of YCOB, LCOB, NdLCOB and YCB.

ii. To grow single crystals of YCOB, LCOB, NdLCOB and YCB.

iii. To characterize the grown crystals for studying their structural, thermal, mechanical, optical and SHG properties.

In the present investigation, the growth of YCOB single crystals was carried out by flux technique for the first time. Two different fluxes - lithium carbonate and boron-tri-oxide were used to grow YCOB single crystals. The grown YCOB crystals were subjected to various characterization techniques and its properties were studied. The YCOB single crystals were
irradiated with Ag$^{9+}$ ions with high energy (120 MeV) and at varying fluences for the first time. The irradiations were carried out both at room temperature and at liquid nitrogen temperature (LNT). The effect of irradiation on the YCOB single crystals was analyzed.

Single crystals of LCOB and NdLCOB were grown from their respective melts. The characterization studies were performed on both the crystals. The IR laser emission at 1064 nm from the NdLCOB crystals were successfully demonstrated.

A new borate based NLO crystal – YCB was synthesized and grown successfully. The characteristics of the grown crystals were analyzed through various characterization studies.

The thesis presents a concise report on the growth of borate based single crystals for NLO and laser applications, by flux and melts techniques and their characterization.