CHAPTER 1

INTRODUCTION TO CRYSTAL GROWTH AND
NONLINEAR OPTICS

1.1 INTRODUCTION

Over the recent years materials science has become an independent
discipline in its own right owing to the rapid development of new materials.
Crystal growth has evolved as an important area of materials science and has
been developed along with the technological advancement in the 20th century.
The rapid advances in microelectronics, communication technologies,
medical instrumentation, energy and space technology were only possible
after the remarkable progress in fabrication of large, rather perfect crystals
and of large-diameter epitaxial layers. Further progress in crystal growth
technology is required for significant contributions to the energy crisis. High-
efficiency white light-emitting diodes for energy-saving illumination and
photovoltaic/thermo-photovoltaic devices for transforming solar and other
radiation energy into electric power with high yield depends on significant
advances in crystal growth and epitaxial technology. Also, the dream of laser
fusion energy and other novel technologies can only be realized after
appropriate progress in the technology of crystal and epilayer fabrication. The
search for new materials and their single crystal growth have now become a
top priority in the scientific development. Inspite of the considerable research
efforts, the growth of reasonably good quality single crystals is still regarded
as a fine combination of science, engineering and technology (Chernov 1984,
Arend and Hulliger 1989).
1.2 CRYSTAL GROWTH

Crystal growth is the major part of a crystallization process, after the nucleation stage. It occurs from the addition of new atoms, ions, or polymer strings into the characteristic arrangement, or lattice, of a crystal. The crystallization process consists of two major events, nucleation and crystal growth. Nucleation can be either homogeneous, without the influence of foreign particles, or heterogeneous, with the influence of foreign particles. Nucleation is the step, where the solute molecules dispersed in the solvent start to gather into clusters that becomes stable under the current operating conditions. These stable clusters constitute the nuclei. However when the clusters are not stable, they redissolve. Therefore, the clusters need to reach a critical size in order to become stable nuclei. Crystal growth is the subsequent development of the nuclei that succeed in achieving the critical cluster size. Nucleation and growth continue to occur simultaneously while the supersaturation condition exists. Crystal growth techniques generally fall into three categories such as solid-solid (solid growth), liquid-solid (solution growth, melt growth) and gas-solid (vapour growth) based on the nature of phase transitions.

Supersaturation is the driving force of the crystallization; hence the rate of nucleation and growth is driven by the extent of supersaturation of the solution. Depending upon the conditions, either nucleation or growth may be predominant over the other, and as a result, crystals with different sizes and shapes are obtained. Once the supersaturation is exhausted, the solid-liquid system reaches equilibrium and the crystallization is complete, unless the operating conditions are modified from equilibrium so as to supersaturate the solution again. The following methods are adopted to attain the supersaturation (i) slow cooling, (ii) solvent evaporation and (iii) gradient transport. Supersaturation can be obtained by lowering the temperature as the
solubility of many materials decreases with temperature. In the present study slow cooling method was adopted for crystal growth. In this method, the high temperature solution containing the components of the materials to be grown and the appropriate solvent are taken in a suitable crucible. The temperature of the furnace is raised to a value slightly above the saturation point for a sufficient time to ensure complete homogenization. Then the solution is cooled at a slow rate through the temperature range, where the desired crystals is required to precipitate. Perfect crystals would only grow exceedingly slowly; real crystals grow comparatively rapidly because they contain dislocations, which provide the necessary growth points. Real crystals are finite and contain defects but nevertheless have long range order, and it is this order which gives crystal their unique properties (Brandle 1979, Brice 1986). The general rule is that the slower the growth rate the better and larger the crystals. Crystals usually nucleate at the coolest point in the crucible. It is preferable that nucleation be confined to a single site. This site will be the sink for subsequent growth, and the crystals obtained.

There is a large variety of methods available for growing crystals. The choice of the method depends on the physico-chemical properties of the material. Solution methods of crystallisation are probably the simplest. For the crystal growth from solution, the solubility of the sample in various solvent systems is one of the first chemical properties to be explored. If heating methods are selected for growing crystals, the thermal stability and melting point of the sample should be determined. As the present work deals with the growth of high temperature melting oxide crystals, a description of high temperature solution growth technique is provided.

1.2.1 High Temperature Solution Growth

To produce large crystals, many ‘bulk growth’ techniques have been developed in which the required material was slowly cooled through its
melting point, either by moving the container through steep temperature
gradient or by slow withdrawal of seed crystal from the melt surface (Pamplin
1980). In high temperature solution growth, the constituents of the material to
be crystallized are dissolved in a suitable solvent, the flux, and the
crystallization occurs as the solution becomes critically supersaturated (Elwell
and Scheel 1975). Recently, number of investigations, have been made on this
technique (Rajeev Bhatt et al 2007, Aravazhi et al 2005, Bordui et al 1987,
The principal advantage of using a solvent is that crystal growth occurs at a
lower temperature than that required for growth from the pure melt. In this
method the growing crystal is not exposed to steep temperature gradients and
the crystal can grow free from mechanical or thermal constrains. This in
combination with the relatively lower growth temperature often results in
better quality crystals with respect to point defects, dislocation densities and
low angle grain boundaries compared to the crystals grown from their direct
melt (Elwell and Scheel 1975).

The reduction in crystallization temperature is advantageous for

1. incongruently melting materials - which decompose before
   melting so that crystallization from melt results in some other
   phase,
2. phase transition materials - in which phase transition causes
   severe strain or even fracture,
3. materials having high vapor pressure at the melting point,
4. materials which have very volatile constituent and hence
   changes in chemical composition and
5. highly refractory materials, which require complicated or
   sophisticated techniques for crystallization from the melt.
It is important to select a suitable solvent or flux for obtaining good crystals from high temperature solution growth. The desirable properties of the ideal solvents are

(i) high solubility for the crystal constituents
(ii) the required crystal phase should be the only stable phase
(iii) low melting point, low volatility at elevated temperatures and low toxicity
(iv) low viscosity and appreciable solubility change with temperature and
(v) low reactivity with the crucible wall and easily available with low cost

There is no ideal solvent which fulfills all these properties and a compromise is necessary to select a suitable solvent by considering the material properties and growth techniques to be adopted. It is advisable to use self fluxes, which have a common cation or anion with respect to the growth materials.

1.2.2 Top Seeded Solution Growth (TSSG)

In TSSG, the crystals can be grown at the surface of the solution when the surface temperature is lower than that of the bottom of the solution and large crystals are grown by using seed crystals of a particular orientation. Orientation of the seed crystal plays a vital role in TSSG technique (Sasaki et al 1993, Kim et al 1995). The rotations of the seed crystals play an important role in homogenizing the growth solution by forced convection. High quality seed crystals with the required crystallographic orientation are necessary with respect to low impurity incorporation and high stable growth rate. The seeds are mounted on the seed rod by using platinum wire and are
slowly introduced into the saturated solution. The presence of seed crystals during the slow cooling process helps in the growth of the crystal in the supersaturated solution. The temperature gradient has to be small and the growth temperature has to be continuously lowered by slow cooling the solution.

The rotation of the seed crystal helps the convection in the melt thereby reducing the formation of nucleation elsewhere. The rotation of the crucible also helps in the enhancement of the growth rate. The temperature control requirements necessary for stable and homogeneous growth are much more stringent than those necessary to prevent spontaneous nucleation. If the temperature of a supersaturated solution is held constant for a long time, the small crystallites will be dissolved and the size of the larger crystallites will increase. In TSSG the crystal dips into the solution, the temperature gradient at the interface is less steep than in Czochralski growth, and this encourages the faceting, which is normally observed in TSSG-grown crystals.

1.2.3 Equipment Required for HTS Growth

The equipment such as (i) high temperature furnace having desired temperature gradient, (ii) precise and programmable temperature controllers and (iii) suitable crucible material are essential to grow large size single crystals by TSSG. Of the various types of heating, only two common heating sources such as resistive heating and induction heating are used for the growth of high temperature oxide crystals. The advantage of resistive heated furnaces over other types is greater electrical efficiency and therefore the temperature control of the furnace can be easily accomplished without the need for elaborate control equipment. Owing to the slow growth rates in flux growth, in order to grow good quality single crystals free of solvent inclusion, the temperature of the furnace has to be maintained with good stability and cooled at very slow and controlled rates. The selection of an ideal crucible is
also an important factor in the case of flux growth. It should be resistant to contamination by the solvent, solute and vapors at the high growth temperatures. Further requirements are a high mechanical strength, ease of cleaning, good thermal shock resistance, reasonably long life time and low cost. For highly corrosive materials, noble metals like Platinum, Rhodium, Iridium and their alloys are normally used as crucibles.

1.2.4 Temperature Profile of the Furnace

During the crystal growth process there is a possibility of multi-nucleation at the walls of the crucible. To reduce the multi-nucleation the temperature profile of the furnace has to be maintained. In the case of borate crystal growth, large size crystals are preferred along the vertical direction. The optimum temperature profile for the growth of crystals is achieved by adjusting the individual temperature zones in the furnace.

1.3 NONLINEAR OPTICS

The second harmonic generation experiment of Franken et al (1961) marked the birth of the field of nonlinear optics. They propagated a ruby laser beam at 694.2 nm through a quartz crystal and observed ultraviolet radiation from the crystal at 347.1 nm. Harmonic generation of electromagnetic waves at low frequencies had been known for a long time. Harmonic generation of optical waves follows the same principle and should also be observable. Yet an ordinary light source is too weak for such an experiment. It generally takes a field of about 1 kV/cm to induce a nonlinear response in a medium. This corresponds to a beam intensity of about 2.5 kW/cm². A laser beam is therefore needed in the observation of optical harmonic generation.
Second harmonic generation is the first nonlinear optical effect ever observed in which a coherent input generates a coherent output. But nonlinear optics covers a much broader scope. It deals in general with nonlinear interaction of light with matter and includes such problems as light-induced changes of the optical properties of a medium. However, observation of nonlinear optical effects requires the application of lasers. Numerous nonlinear optical phenomena have been discovered since 1961. They have not only greatly enhanced our knowledge about interaction of light with matter, but also created a revolutionary change in optics technology.

Each nonlinear optical process may consist of two parts. The intense light first induces a nonlinear response in a medium, and then the medium modifies the optical fields in a nonlinear way. Non-linear-optical effects are analyzed by considering the response of the dielectric material at the atomic level to the electric fields of an intense light beam. In order to describe more precisely what we mean by an optical nonlinearity, let us consider how the dipole moment per unit volume or polarization \( P \) of a material system depends on the strength \( E \) of the applied optical field. In the case of linear optics, the induced polarization depends linearly upon the electric field strength in a manner that can often be described by the relationship.

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

where \( \varepsilon_0 \) is the permittivity of free space and \( \chi^{(1)} \) is known as the linear susceptibility which is responsible for the linear optical properties such as absorption, index of refraction, dispersion and birefringence of the medium. When the applied electric field strength is high enough and comparable to the inter-atomic field, the amplitude of the dipoles does not faithfully reproduce
the exact sinusoidal electric field. Indeed, it produces the distorted reradiated wave, which contains the induced polarization given by

\[ P = \varepsilon_0 \chi^{(1)}.E - \chi^{(2)}.E.E + \chi^{(3)}.E.E.E + \ldots \]  

(1.2)

where \( \chi^{(2)}, \chi^{(3)} \) known as the second and third order nonlinear susceptibilities and their magnitude decreases as their order increases (\( 10^{-5}:10^{16} \) and so on). The second order susceptibility term \( \chi^{(2)} \), gives rise to second harmonic generation, frequency mixing and parametric generation, while the third order susceptibility \( \chi^{(3)} \) is responsible for the third harmonic generation, stimulated Raman scattering, optical bistability and phase conjugation. Nonlinear optical susceptibilities are characteristic properties of a medium and depend on the detailed electronic and molecular structure of the medium.

Figure 1.1 Linear and nonlinear response of polarization \( P \) to an applied electric field \( E \).

For positive and negative fields, the response of the optical medium is not symmetrical in the case of nonlinear response (curved line: Figure 1.1).
In this case, the negative field \( E_0 \) produces a greater polarization than a positive field of the same magnitude.

The easiest way for generating the new frequencies that are not available with the existing laser sources is by performing the lower order nonlinear responses. It can be shown that the second order term makes no contribution to the polarization in isotropic optical materials or one having a center of symmetry. A crystal having a center of symmetry is characterized by an inversion center, such that if the radial coordinate \( r \) is changed to \(-r\) the crystals atomic arrangement remains unchanged and so the crystal responds in the same way to a physical influence. Thus we should have both

\[
P_2 = \chi^{(2)} EE, \quad -P_2 = \chi^{(2)} -E -E
\]  

(1.3)

Because the electric field is squared \( P_2 = -P_2 \) which can be true only if \( P_2 = 0 \). In such a crystal, reversing the applied field should not except for a change in sign-change any physical property such as polarization. Crystalline materials lacking inversion symmetry can exhibit a so-called \( \chi^{(2)} \) nonlinearity. In such a nonlinear crystal, sum frequency generation (SFG) or difference frequency generation (DFG) can occur, where two pump beams generate another beam with the sum or difference of the optical frequencies of the pump beams. Such a process requires phase matching to be efficient, and usually there is no simultaneous phase matching for sum and difference frequency generation. A special case is sum frequency generation with an original pump wave and a frequency-doubled part of it, effectively leading to frequency tripling. Such a cascaded process can be much more efficient than direct frequency tripling on the basis of a \( \chi^{(3)} \) nonlinearity.
Difference frequency mixing with pump waves of similar frequency can lead to a mixing product with a long wavelength. This is sometimes used for generation of mid-infrared beams or even terahertz waves. In a sum frequency mixer, both pump waves experience pump depletion when the signal becomes intense. In a difference frequency mixer, however, the lower-frequency wave is amplified. This is because photons of the beam with highest photon energy (shortest wavelength) are effectively split into two lower-frequency photons, thus adding optical power to both lower-frequency waves. The term parametric amplification emphasizes the aspect of amplification, and the difference frequency mixing product is then called the idler wave.

In second harmonic generation, two identical photons from a single pump beam are added and result in a photon having twice the frequency. The generation of second harmonic rays from the incident wave of frequency $\omega_1$ is involved as a two step process. First, a polarization wave at the second harmonic frequency $2\omega_1$ is produced, whose phase velocity and wavelength are determined by the refractive index of the fundamental wave $n_1$, that is $\lambda_p = c/(2\nu_1 n_1)$. The next step is the transfer of energy from the polarization wave to an electromagnetic wave (em) at frequency $2\omega_1$, whose wavelength and phase velocity are determined by the refractive index of the second harmonic wave $n_2$ that is $\lambda_2 = c/(2\nu_1 n_2)$. For the attainment of efficient frequency conversion and sustained growth in SHG, the phase velocities of the fundamental and the second harmonic waves must be equal. This leads to the phase matching condition, which can be written as $n_1 = n_2$, where $n_1$ and $n_2$ are the refractive indices for the fundamental and second harmonic waves respectively. If the crystal is phase matched the power generated will be large. If the interaction is not phase-matched, the power shuttles back and forth between the generated wave and the input waves and so very little power is
obtained. Due to the birefringing nature of the medium in optical region, the phase mismatch ( \( \Delta k \) ) between the polarization and em waves is given by

\[
\Delta k = \frac{4\pi}{\lambda_1} (n_1 - n_2)
\]  

(1.4)

The fact that the dispersion of the phase velocities of both the waves in the nonlinear optical medium can be offset by using the natural birefringence of the medium is utilized for attaining the zero-mismatch. There are various methods available for attaining the zero mismatch like index phase matching, temperature and angular phase matching. In index matching, by choosing an appropriate choice of polarization and propagation direction, it is often desirable to obtain \( \Delta k = 0 \) by varying the birefringence of the medium. This is done by choosing the direction in the crystal such that the refractive index of the second harmonic wave \( n_2 \) for the extraordinary ray equals \( n_1 \) for the ordinary ray. In temperature tuning, by changing the temperature of the medium it is possible to change the birefringence of the extraordinary wave as its index of refraction is temperature dependent. In general the extraordinary wave is more temperature dependent than the ordinary wave. Whereas, in the case of angle tuning, by changing the angle between the wave normal and optic axis, the refractive index of the extraordinary wave varies and equals to the refractive index of the fundamental wave and hence leads to the exact phase matching. Moreover, if the phase matched direction coincides with one of the optic axes then it is called as non-critical phase matching. Whereas, in the case of critical phase matching, the phase matched direction does not coincide with an optic axis.

Depending on the possible orientations of the linear polarization of the incident radiations, phase matching is classified into type I and type II. When the two input pump waves having the same polarization of frequency
ω₁, combine to form a wave with frequency 2ω₁ it is called type I phase matching,

\[ 2n_e^{ω} = n_o^{2ω} \]  \hspace{1cm} (1.5)

On the other hand, if the polarization of the pump waves is orthogonal to each other then it is called as type II phase matching,

\[ n_o^{ω} + n_e^{ω} = 2n_o^{2ω} \]  \hspace{1cm} (1.6)

The conversion efficiency mainly depends on the crystal length (l), power density and phase mismatch (Δk). For a crystal of fixed length, the second harmonic generation strongly depends on the phase mismatch (Δk).

1.3.1 Laser Parameters

High second and third harmonic conversion efficiency mainly depends on the laser parameters such as (i) power density, (ii) beam divergence, (iii) spectral linewidth and (iv) spectral brightness.

1.3.2 Absorption

Absorption in the crystal during the conversion efficiency measurements leads to thermal gradients as well as thermally induced stresses. Thus the associated refractive index variation severely restricts the crystal volume over which phase matching can be achieved. Also, in high power laser experiments, generation of heat inside the medium due to absorption is catastrophic to the crystal. A self-induced thermal distribution in the nonlinear medium can be caused by absorption of the fundamental or harmonic beams or multi-photon absorption processes.
1.3.3 Nonlinear Optical Coefficient

From the theoretical considerations, it is seen that the crystal with highest nonlinear optical coefficient would be the most desirable material in frequency doubling experiments. However, in practical situations, it turns out that other parameters such as laser damage resistance, optical quality, angular and thermal tuning ranges and acceptance angle etc. are also equally important parameters. A material with low NLO coefficient with long interaction length can be as efficient as a short crystal with a high NLO coefficient.

1.4 OVERVIEW OF NONLINEAR OPTICAL MATERIALS

The field of NLO and photonics are rapidly emerging as the technology for the 21st century. The discovery of optical second harmonic generation in crystals by Franken et al (1961) spurred rapid progress in nonlinear optics. In the early stage of nonlinear optical developments, NLO devices were limited to harmonic generation, parametric amplification and oscillation in the visible and infrared regions. This prompted the researchers to search for new nonlinear optical materials with better nonlinear properties for the UV region. Of the several hundred NLO materials, some of them such as potassium dihydrogen phosphate (KDP), lithium niobate (LiNbO3), potassium niobate (KNbO3), potassium titanyl phosphate (KTP), recently developed borate crystals crystals find wide NLO applications for UV generation. For the purpose of reliable laser frequency conversion, NLO crystals need to have properties like:

1. large NLO coefficient
2. moderate birefringence
3. small walk-off effect
4. large angular spectra and temperature bandwidths
5. wide transparency range for operating wavelength 
6. high laser-induced damage threshold 
7. ease of growth 
8. low material cost 
9. good chemical stability and 
10. good mechanical stability.

Until 1975, most NLO crystals were based on the P-O, I-O and Nb-O bonds like those in KDP (KH₂PO₄) LiIO₃ and LiNbO₃. LiNbO₃ is the most extensively studied material for device applications involving the linear electro-optic effect, but it suffers from degradative photorefractive effects which restrict its use in various applications. KDP has been used widely for phase matched SHG of high-powered near-IR lasers. It is particularly suitable for the purpose of a laser fusion system involving NLO devices with large dimensions of several tens of cm. Likewise, because of properties (1), (2) and (9), crystals like LiNbO₃ and KNbO₃ are frequently use for frequency conversions for semiconductor lasers. The KTP (KTiOPO₄) crystals developed later provide properties that merely combined those of KDP and LiNbO₃. This makes KTP popular for both high power and semiconductor laser operations. Taking the advantage of large angular acceptance of KTP family crystals, tunable infrared lasers have been shifted into the visible region by sum frequency generation and into the mid infrared region by difference frequency generation. Among the available materials, borate crystals have risen to prominence in the last twenty years due to their large angular and temperature phase matching bandwidths along with their large optical damage resistance for 1064 nm Nd:YAG laser sources. Because of the relatively high resistance against laser-induced damage and higher transparency in the UV region, NLO crystals with B-O bonds are often employed for high-power UV light generation.
The monochromatic and coherent photon flux of laser light is viewed as a clean energy source for the synthesis and processing of materials, because of their high photon energies and ability to tightly focus radiation at short wavelengths. For instance, photon energy in the UV region is sufficient to induce bond-breaking processes in many materials. Because of the intrinsically short upper laser lifetime of UV laser active media and the requirement of intensive electron pumping to the excitation state, direct lasing from the solid-state medium is challenging. An effective method of producing UV generation is cascading the sum frequency generation pumped by the output of near – IR (1μm) solid state lasers, by using nonlinear optical crystals (Sasaki et al 2000). Though other NLO crystals like KTP find wide applications in frequency conversion, optical parametric oscillation and electro optics, application of these materials in ultraviolet region is not possible because their UV cut off is around 350 nm. Hence, scientists put forth their attention to find new NLO materials capable of generating UV light radiation.

Borate family crystals with B-O bonds have been identified as suitable crystals which have received much attention because of their excellent properties like high resistance against laser-induced damage and higher transparency in the UV region (< 200 nm) (Chen et al 1989, Mori and Sasaki 1999). Various borate crystals, including β-BaB₂O₄ (BBO), LiB₃O₅ (LBO), CsB₃O₅ (CBO), CsLiB₆O₁₀ (CLBO), BiB₃O₆, KBe₂BO₃F₂, Sr₂Be₂B₂O₇, GdCa₄O(BO₃)₃, YCa₄O(BO₃)₃, GdₓY₁₋ₓCa₄O(BO₃)₃, K₂Al₂B₂O₇ and BaAlBO₃F₂ and the latest Ca₄LnO(BO₃)₃ (CLnOB, where Ln = Gd, La, Y), have been studied as promising NLO crystals.

Cesium triborate (CsB₃O₅) has been identified as a good nonlinear optical material because of its wide transparency in UV region and high optical damage threshold compared to other inorganic oxide crystals. These
unique properties combined with its mechanical hardness, chemical stability and non-hygroscopicity make CBO attractive material for third harmonic nonlinear optical generation. For type II THG the effective nonlinear coefficient of CBO is close to its maximum. Therefore CBO can outperform LBO in 355 nm generation. CBO crystals can be grown from stoichiometric melts and from flux growth method.

1.5 SCOPE OF THE THESIS

The present work is aimed at the growth of nonlinear optical CsB₃O₅ single crystal and the improvement of its optical properties for high power UV generation.

Growth of CBO crystal by top seeded solution growth (TSSG) from self-flux solutions is presented. The main problems during the growth of CBO crystals like multi-nucleation and breaking of seed during growth have been reduced. Large size crystals of size 50 x 45 x 45 mm³ (a x b x c) and weighing 159 g has been grown using TSSG from a 74 mol% B₂O₃ solution.

Studies pertaining to the scattering centers in CBO crystals have been performed. CBO crystals grown from 74 mol% B₂O₃ solutions have scattering centers. Scattering centers in nonlinear optical crystals significantly restrict device performance by causing optical loss, crystal damage, etc. Therefore, the evaluation of light scattering in CBO is indispensable for high-power laser applications. The reason for the formation of scattering centers in CBO crystals was studied and the scattering was considerably reduced by various experimental techniques like post growth quenching and vapour transport equilibration techniques. From the studies the presence of retrograde solid solution region in CBO has been determined. Based on the hypothesis of retrograde solid solution curve, we are able to explain the mechanism of scattering centers and green luminescence formation in CBO crystals.
The improvement of laser induced damage threshold (LIDT) in CBO crystals and the reduction of surface degradation have been studied. Because of the deliquescence property the surface of the CBO crystals gets degraded in normal atmospheric conditions. After in-depth analysis the proper condition for maintaining the surface of the crystal was determined. The LIDT of the CBO crystals has been increased by fast cooling the crystals after growth. The second harmonic generation and high power third harmonic generation have been studied using CBO crystals.