

CHAPTER 1

AN OUTLINE TO THE CRYSTAL GROWTH FROM SOLUTION AND LASER CRYSTALS

1.1 INTRODUCTION

It is more appropriate to say that today man lives on 'Materials Age'. The rapid development of new materials has made the Materials Science discipline highly interdisciplinary. Crystal Growth is an important field of Materials Science, which involves the control of phase change. Generally matter exists in three states namely solids, liquids and gases with different degree of atomic or molecular mobility. The solid state materials can be further classified as single crystals, polycrystals and amorphous materials depending upon the arrangement of constituent molecules, atoms or ions. An ideal crystal may be defined as the solid in the most ordered form, i.e. single crystal is an infinite lattice of atoms arranged in patterns, which repeat in all three dimensions, with repeat distances. However, real crystals are finite and contain defects, but nevertheless have long range order, which gives their unique properties. It is obvious that the preparation of single crystal is more difficult than the preparation of polycrystalline material and the extra effort is justified because of outstanding advantages of single crystals than polycrystalline material. The chief merits of the single crystals are the anisotropy, uniformity of composition and the absence of boundaries between the individual grains which are inevitably present in polycrystalline material.

At one time natural specimens were the only source of large well-formed crystals which are not sufficient to cater to the need for utilitarian purposes and for further study. Hence, attempts were made to synthesize monocrystals artificially through the knowledge gained from continuous and systematic investigations. At present crystal growth has become an industrially important field of research. Today several hundred application oriented single crystals are being grown by employing various techniques. Though it is very difficult to present the wide range of crystal growth methods, techniques and theories in the form of single monograph or book, several authors have attempted to give an outline to the most of the crystallization techniques [1-11]. However, numerous reviews, monographs, and books are available specialised in each section of the crystal growth, such as Faktor and Garrett on Vapour growth [12], Elwell and Scheel on high temperature solution growth [13], Henisch on gel growth [14], Brice on melt [15] and Buckley on solution growth [16]. Apart from these in the literature, several series of books are being published such as Springer - Verlag under the title "Crystals" (Ed. Freghardt), North Holland series 'Current topics in Materials Science (Ed.E. Kaldis), Consultants Bureau Enterprise, Inc's series on "Growth of Crystals" (Ed.A.V. Shubnikov and N.N. Sheftal) etc.

Crystal growth involves the control of phase change. On the basis of this it may be classified into three categories as follows:

- Solid growth - Solid to solid phase transitions.
- Liquid growth - Liquid to solid phase transitions.
- Vapour growth - Gas to solid phase transitions.

In the above mentioned categories liquid growth includes both melt and solution growth. Melt growth is the most straight forward technique, whereas in the solution growth the liquid phase may contain deliberately added foreign material in the solution as a solvent.

There are numerous growth techniques available in each category. The selection of any crystal growth method depends much on the properties of the materials to be crystallised and to a greater extent on the growth kinetics, requirements such as size, shape, purity, economics, etc. Brief outline on various important techniques of crystal growth from solution has been presented in this chapter.

1.2 GROWTH FROM SOLUTION

In this process, a saturated solution of the material in an appropriate solvent is used, from which growth takes place after the solution is critically supersaturated. Growth from solution is more widely used than the growth from melt or from vapour phase. Growth of crystals from solution can be classified into low and high temperature solution growth methods based on their temperature of operation. The general principle of crystal growth from solution is common to both low and high temperature solution growth methods. Hence, all the methods applied to the low temperature are available for high temperatures also. Several books and reviews have been written by various authors on solution growth from time to time [17-19].

1.3 SEQUENCE OF CRYSTALLISATION FROM SOLUTION

Crystallisation from solution can be sequenced as preparation of saturated solution, achievement of supersaturation, nucleation and growth of crystals.

1.3.1 Preparation of saturated solution

A solution that is in equilibrium with the solid phase is said to be saturated with respect to that solid. There is nothing to discuss the process of preparing solution except that the finer the substance lesser the time of dissolution. Stirring and vigorous shaking helps to promote a rapid mixing of the solid and liquid components. However they have no influence on the amount of solid material that a given solvent can take in, but this varies from one temperature to another. Hence, a plot representing saturation of solvent at different temperature, which is known as a solubility curve can be drawn for any particular solute-solvent system. The solubility data for numerous inorganic materials in water have been presented by Mullin [20]. Though determination of solubility in high temperature poses many challenges to the researchers, several reports have been published on the solubility of sesquioxides in $\text{PbO-PbF}_2\text{-B}_2\text{O}_3$ melt [21-23].

The knowledge about phase diagram of the desired material with respect to temperature is also essential. In practice numerous methods such as Quenching method, Hot stage microscopic observation method, Differential Thermal Analysis(DTA) [24,25] and Thermo Gravimetric(TG) method have been used for the determination of phase of the growing crystal. Among the available methods DTA and TG are being widely used to understand the growth mechanism [26] growth rate [27] apart from the identification of phase of the growing crystal. The phase diagrams of several hundred inorganic compounds have been compiled by Levin et al [28].

1.3.2. Achievement of supersaturation

Growth of crystals from solution requires the production of supersaturated solution at the growing face. The methods commonly used to attain supersaturation condition in both low and high temperature solution are slow cooling, controlled evaporation and temperature gradient technique.

(a) Slow cooling technique

This technique requires very sensitive and accurate temperature controllers and programmers to perform the cooling process. In practice this method is widely used with great success. For unseeded growth, Laudise [3] derived an expression for linear growth rate as

$$R = \frac{v}{\rho A} \left(\frac{dn_e}{dT} \right) \left(\frac{dT}{dt} \right) \quad (1.1)$$

where v is the volume of the solution
 A is the area of the growing crystal
 ρ is the density of the crystal
 dn_e/dT is the change in solubility with temperature
 and dT/dt is the cooling rate.

This equation(1.1) holds good only when all the solute precipitated is deposited on the crystal.

The general rule to adopt the cooling rate is, that the slower the growth rate better and larger the crystals. However, one has to find a compromise between cooling rate and the duration of experiment. The major advantage of this

method is that closed or sealed crucibles/containers can be used. Hence, highly volatile or even toxic materials can be grown. But sealing the crucible makes it difficult to provide conventional stirring and top seeding systems. Several alternative techniques for effective stirring[29,30] and seeding[31,32] have been developed and used successfully to grow variety of large size crystals.

(b) Evaporation technique

This technique is the basis of common salt production for thousands of years and has been frequently used in crystal growth from high temperature solution. Several systematic studies on this technique have been made by Grodkiewicz and Nitti [33] and Wood and White [34].

This method essentially requires the basic apparatus as in the case of slow cooling technique except cooling programmers. Since the solvent evaporation may be carried out isothermally, this method has several advantages connected with growth at constant temperature which may be listed as follows.

1. Easy and often closer temperature control
2. Constant concentration of equilibrium defects
3. Approximately constant incorporation of solvent ions as impurity
4. Homogeneous incorporation of dopants.

The main disadvantages are

1. It is difficult to control the rate of evaporation which ultimately affects the quality of the crystal.
2. Proper care should be taken to protect from the attack of highly poisonous or corrosive vapours, which is difficult to achieve. Hence, it is preferable to use only non toxic materials.

This is the only method which can be used with materials having very small temperature coefficients of solubility and also useful for the materials with negative coefficients.

(c) Temperature gradient technique

This method relies on the transport of materials from a hot region containing source materials to be grown to a cooler region by transporting the solution using either natural or forced convection, where the solution is supersaturated and the crystal grows.

For a given solute-solvent system the mass transport rate and hence the supersaturation and growth rate may be varied by adjusting temperature difference, the area and form of seed and nutrient and the depth of the solution. The advantages of this method are economy of the solvent and the advantages arising due to constant temperature growth. This method is relatively insensitive to changes in temperature provided both the source and the growing crystal undergo the same change. On the other hand, changes in the small temperature difference between the source and the growing crystal have a large effect on the growth rate.

Apart from the above mentioned three popular methods there are a few special methods to obtain supersaturation such as reaction technique, in which solute constituents formerly separated diffuse to the region where reaction (and crystallisation) proceeds. Recently Tolksdorf and Welz [35,36] described a new technique in which the advantages of seeding, ACRT (Stirring) and temperature gradient transport are combined together.

1.3.3. Nucleation

The initial stage of crystallisation in a supercooled or supersaturated liquid is the formation of nuclei of the crystalline phase by joining few atoms or molecules together. Nucleation like an ordinary chemical kinetics, involves an activation process leading to the formation of unstable intermediate state known as 'embryo' [37]. At this stage the embryo may continue to grow or tend to dissolve. Once the embryo attains a critical size, there is more probability for it to grow further. Generally nucleation has been classified as primary nucleation and secondary nucleation. The term primary is reserved for homogeneous nucleation and heterogeneous nucleation. The formation of nuclei by atoms or molecules in the interior of the parent system is referred as homogeneous nucleation and if it occurs on a foreign atom or surface of the container or any other imperfections it is referred as heterogeneous nucleation. If the nucleation occurs in a supersaturated solution in which no crystalline matter is present it is termed as primary nucleation, whereas if nucleation occurs in the vicinity of the crystals, it is termed as secondary nucleation. Nucleation can often be induced by external influences like agitation, mechanical shock, friction, environmental factors and X-rays, γ rays, UV irradiation

etc. [38,39]. An extensive review on nucleation has been presented by several workers from time to time [40-43].

1.3.4. Growth of crystals

Once critical nuclei are formed, they grow into crystals of macroscopic sizes with well developed faces. Several theories based on different concepts like surface energy, diffusion and surface adsorption etc have been proposed to explain the mechanism of crystal growth. The first two theories are more of historic importance and the third theory was proposed by Volmer [44] in 1922. According to this theory, a molecule arriving at a crystal surface from the bulk of the supersaturated solution or supercooled melt loses a part of its latent heat. But the molecule has sufficient energy to move along the surface of the crystal. All molecules similar to this move along the surface and collide with each other, either elastically or inelastically. Due to inelastic collision these molecules join together and form a two dimensional crystal.

Kossel [45] considered the crystal growth from atomistic consideration rather than thermodynamic functions. He assumed that the attachment energy of a growth unit on a growing surface is a simple function of distance only. Integration of atoms or growth units into the crystal will occur most readily at vacant sites or 'Kinks' along the edge of this layer.

Though the concept of two dimensional growth theory seems to be more practicable model, it fails completely, when applied to the real systems having low supersaturation. To overcome this difficulty Frank [46] first introduced a novel concept that the growing faces have many spirals.

These spirals have their origin at the screw dislocation points and produce steps. The step originating from a screw dislocation winds itself into a spiral around that point. The molecules that are adsorbed on the surface, diffuse into the kinks. The growth process continues for ever since the spiral would be renewed and thus removes the necessity of nucleating a new layer. In practice, spirals have been observed on variety of materials by several researchers [47-50].

Recently an interesting theory named as mixed cluster theory has been proposed by Wanklyn [51] based on Goodman's model for glasses. The formation of complexes in the solution due to interactions of solute-solvent, solute-solute and solvent-solvent has been already established by the earlier workers. This mixed cluster theory proposed by Wanklyn based on the formation of clusters explains the role of additives on the nucleation and growth kinetics. According to this theory the nature and behaviour of the clusters decide the various parameters in crystal growth from solution such as viscosity, rate of nucleation, growth rate etc.

1.4. PRACTICAL ASPECTS OF SOLUTION GROWTH

The success of crystal growth from solution depends to a greater extent on the proper choice of the growth technique and appropriate solvent system. Each technique has its own advantages and limitations. Hence, selection of the growth technique can be made on the basis of desired material properties and requirements such as quality, size, economy etc.

1.4.1. Choice of solvent

The wide variety of materials crystallised from solution makes a generalised discussion of an ideal solvent difficult. However, important criteria for a good solvent are listed below

1. High solubility and moderate reversible solubility of desired material.
2. Positive temperature coefficient of solubility (Negative coefficient creates problems with stability and large positive one requires very precise temperature controllers).
3. The crystal phase required should be the only stable solid phase.
4. Small vapour pressure at the growth temperature unless an evaporation technique is used.
5. Viscosity should be low in the range of 1 to 10 centipoise.
6. Non corrosiveness with container and stirrer.
7. Low tendency of the solvent to 'creep' out of the container or crucible.
8. Low toxicity
9. Non flamability
10. Ready availability in high purity at low cost.

In the case of high temperature solution growth additional criteria for the selection of solvent are

1. Low melting point
2. Ease of separation from the grown crystals by chemical or physical means.

There is no solvent which fulfils all these ideal properties and a compromise is always necessary, depending on the type of the crystal and the requirement of size and quality which makes some properties important. Some time, more than one solvent mixed together will serve as a better solvent system.

In low temperature solution growth, water is an excellent solvent for numerous materials. It is however fairly volatile although the problem arising from this can be overcome by putting a film of oil on the surface.

In high temperature solution growth commonly various oxide compounds are being grown. At present the commonly used solvents can be classified as follows.

- (a) Lead and Bismuth compound
- (b) Borates
- (c) Vanadates, molybdates and tungstates
- (d) Alkali halides, carbonates etc.

(a) Lead and Bismuth compound

Lead oxide was rediscovered as a flux by Remeika [52] and applied to the growth of ferrite crystals. The high solubility of refractory oxide in lead containing melt is attributed to the strong polarizability of the Pb^{+2} ions and dissolution is presumably effected by the formation of complex ionic species. $PbO-PbF_2$ system has higher solubility than PbO , which has low eutectic temperature ($500^\circ C$). Nielsen [53] has grown better quality YIG crystals from this flux system. This system still suffers a drawback of high volatility mainly due to lead fluoride which often results in uncontrolled nucleation. Elwell has made' an extensive experimental studies with the aim of understanding the nature of the solvent systems and the role of additives [54-57].

(b) Borate flux

Boron trioxide is not suitable as a solvent due to its high viscosity. The viscosity is greatly lowered when the glassy network is broken by the addition of monovalent metal ions such as alkali ions and the alkaline earth ions. $BaO-B_2O_3$ flux system was advocated by Linares [58] who has grown several iron containing oxides as well as variety of other oxides. The advantages of this system are low volatility, low rate of attack on platinum crucibles and low density compared to lead based flux system. $BaO-BaF_2-B_2O_3$ flux system has been proposed as solvent for rare-earth garnets and orthoferrites by Hiskes et al [59] and its properties are discussed by Elwell et al [60].

1.4.2. Experimental set-up required for solution growth

As discussed earlier, production of supersaturation at the growth face is achieved by either slow cooling or evaporation or temperature gradient method. In practice the supersaturation is being achieved by adopting any of the individual methods or combination of more than one method. Growth of crystals from solution involves highly sensitive and sophisticated instrumentation.

Basically solution growth requires

- a) Heating arrangement to raise the temperature of the solution to growth temperature.
- b) Temperature measuring devices
- c) Temperature controllers and programmers
- d) Solution stirring arrangements
- e) Containers/crucibles and
- f) pure chemicals.

However, the exact requirements for the above mentioned instruments can be decided by considering the properties of the materials to be crystallised and growth techniques to be adopted.

In the case of high temperature solution growth, an arrangement to separate the grown crystals from the solvent has to be provided because in general, crystallisation is terminated with the solution at a temperature above the

eutectic point, and the crystals produced may be separated from the excess solution either at this temperature or following rapidly cooling to room temperature.

The excess of solidified flux is normally dissolved in suitable solvent system. This process is referred as leaching. The great disadvantage of this technique is that the rate of dissolution may be extremely low. Elwell et al [13] have found that the excess $\text{PbO/PbF}_2/\text{B}_2\text{O}_3$ may be dissolved in dilute nitric acid within one or two days if maintained at close to its boiling point. An alternate technique to separate the grown crystals has been suggested by Groudiewicz et al [61], who punctured the crucible from below with steelspike, without removing the crucible from the furnace. The simplest way to remove the excess solution is to remove the crucible with platinum tipped tongs from the furnace and decant the liquid after removing the crucible lid. This method has been used by Wanklyn [62].

An isothermal technique to remove the excess of solution has been used by Kawave and Sawada [63] who after growth of BaTiO_3 from Na_2CO_3 solution at 1173K, sucked up the still liquid flux through the nickel pipe by using rotary pump and then cooled the furnace with the crucible to room temperature.

1.5. ADVANTAGE OF THE SOLUTION GROWTH

The chief advantage of the solution growth results from the fact that the crystals are grown at temperatures well below the melting point. Hence, the detailed knowledge about the desired materials's melting point, melting behaviour and stability in air are not required. Moreover the reduction in temperature is desirable or even

essential for many materials. The following materials can be grown from solution alone.

1. Incongruently melting materials (e.g. YIG) [54-66]
2. Materials which decompose before they melt (e.g. CaCO_3) [67]
3. Materials which have very high vapour pressure at the melting point (e.g. AlF_3 , ZnO) [68,69].
4. High refractory materials for which suitable container is a problem (e.g. MgO) [70].
5. Materials which undergo a phase transition (e.g. ZrO)[71]

Other advantages of crystal growth from solution are based on the fact that the growing crystal is not exposed to steep temperature gradients resulting in better quality crystals free from thermal strains. The added advantage of this method is the presence of facets, which often remove the need for orientation, cutting and polishing.

The disadvantages of the solution growth are the invariable presence of substitutional or interstitial incorporation of solvent ion into the crystal lattice, microscopic or macroscopic inclusions of solvent or impurities, non-uniform doping, a slow growth rate and container problems. However, by selecting proper solvent the incorporation of solvent ion can be minimised and homogeneous doping can also be achieved under adequately controlled conditions.

1.6 LASER MATERIALS

In the year 1960, a couple of years after Schwlow [72] demonstrated the laser action, Maiman [73] had achieved the ever first laser action in practice by using Ruby ($\text{Al}_2\text{O}_3:\text{Cr}^{3+}$) crystalline solid system. Subsequently lasers based upon gases, liquids, glasses and organic dyes have been developed. Though all these lasers are developing considerably, solid state lasers still retain great advantages over other laser media. Striking advances in quantum electronics have been mainly based on the optical quality single crystals. An excellent book on laser crystal and their spectral properties has been written by Kaminskii [74].

Number of lasers have been operated doping several active ions like Rare earth trivalent ions (Nd^{3+} , Eu^{3+} , Pr^{3+} , Ho^{3+} , Ti^{3+}) Rare earth divalent ions (Sn^{2+} , Ti^{2+} , Dy^{2+}) Actinide ions (U^{3+}) and Transition metal ions (Ni^{2+} , Co^{2+}) in various types of insulating oxides, mixed oxides, fluorides, mixed fluorides and few other types of the laser host materials. The extensive use of rare earth energy state is not an accidental choice. The fluorescence spectra of rare earth ions arise from electronic transitions between levels of partially filled 4f shell, which is shielded from the surrounding crystal field by filled 5s and 5p orbitals. Therefore the emission lines are narrow and the position of the 4f levels for a given ion is essentially unaffected by change in host crystal, (i.e) the position of the energy levels is similar to free ions. Despite the shielding, some splitting of the energy levels does occur due to crystal field of the host lattice and the nature of the splitting produces variations in laser performance from one material to another. The actinide ion is similarly

derived from 5f electrons which are partially shielded by 6s and 6p electrons. The shielding being less effective, the nature of the host assumes greater importance. The effect of host material is most apparent for transition metal ions where the unstable energy states are derived from the almost unshielded 3d electrons. The nature and position of these levels are markedly different from the free ion case and are so dependent upon the crystalline field, that the chance of an ion and host combining to give a suitable energy system is very small; hence the restricted number of transition metal ions useful for stimulated emissions. Although absorption and emission spectra generally consist of broad bands reflecting the interaction with lattice vibrations, sharp lines do exist in transitions between certain states whose separations are essentially independent of crystal field for e.g. Cr^{3+} .

Divalent rare earth ions offer two properties which are highly desirable in an optical maser. Strong 4f-5d transitions in the visible and near IR regions provide broad absorption bands for optical pumping and emission takes place in 4f-4f transitions which preserves the sharp lines fluorescence characteristics of the trivalent rare earth ions. An excellent review on laser active ions has been made by L.F. Johnson [75].

1.6.1. Laser host material

The choice of the host material as well as active ion depends, to a certain extent, upon the use of the laser system. For example, a high gain material is favoured for continuous wave operation, to provide low threshold, but a lower gain is preferred for Q-switching in order to prevent the material losing prior to the operation of the switch and

before the required amount of energy has been stored. However, the basic requirements for the crystalline hosts are.

(i) It should form a substitutional solid solution with the active ion at concentration levels which produce reasonable gain. Hence, materials with substitutional lattice sites of similar size and valency to the active ion are obvious choices. These qualities can be obtained only in good single crystals with appropriate doped ions.

(ii) Only mechanically hard material can meet the specifications of laser rods, which can be achieved by cutting, grinding and polishing.

(iii) Chemical stability is important for coating antireflection dielectric layers. Hence, it should be chemically stable.

(iv) It should have low thermal expansion, because during optical pumping due to the dissipation of large amount of heat, the crystal host will be subjected to temperature gradients.

(v) However, a material with high thermal conductivity will help in removal of heat.

(vi) Most materials change refractive index with temperature. Low temperature coefficient of refractive index is preferred.

(vii) The host material must have transparency at the absorbing and fluorescing wavelength of the active ions.

(viii) Ideally the host ion combination should ensure a broad absorption band, so that most of the pumped energy may be used. If the bands are narrow, other species of ions are added to transfer energy from their own absorption bands into those of active ions. This process is nonradiative.

(ix) The quantum efficiency of the host-ion combination should be high which means that a high probability should exist for an absorbed photon to result in the emission of a stimulated photon.

(x) In order to achieve a high gain, the output of the lasing transition should have a minimum spread in frequency, i.e. it should have a narrow line width.

Ideally no material has all the required properties and a compromise has resulted in a large number of host lattice/ active ion combinations. A list of the most commonly used laser host materials and their properties have been presented in Table 1.1. An excellent review on solid state crystalline laser materials was written by Kiss and Pressley [76].

1.6.2 Stoichiometric laser materials

Stoichiometric laser materials are gaining much importance in the field of quantum electronics, integrated optics and laser crystal physics. In these stoichiometric laser materials active ions are dominant components of the crystalline lattice in contrast to the conventional laser materials, in which laser active ions will be dispersed into the host materials. These high-concentration materials are termed as either stoichiometric or self activated laser

Table 1.1. IMPORTANT SOLID STATE CRYSTALLINE LASER SYSTEMS

S.No.	Classification	Host Crystal with laser activator ions
1	Simple oxide	$\text{Al}_2\text{O}_3:\text{Cr}^{3+}$, $\text{Y}_2\text{O}_3:\text{Nd}^{3+}\text{Eu}^{3+}$, $\text{Gd}_2\text{O}_3:\text{Nd}^{3+}$, $\text{La}_2\text{O}_3:\text{Nd}^{3+}$, $\text{Er}_2\text{O}_3:\text{Nd}^{3+}$, Tm^{3+}
2	Oxide-oxide Mixed oxide	$\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Nd}^{3+}$, Ho^{3+} , Er^{3+} , Tm^{3+} , Yb^{3+} , and Cr^{3+} $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Nd}^{3+}$, Ho^{3+} , Er^{3+} , Tm^{3+} YAlO_3 : Nd^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} YVO_4 : Nd^{3+} , Eu^{3+} , Ho^{3+} and Tm^{3+} PbMoO_4 : Nd^{3+}
3	Simple Fluoride	CaWO_4 : Nd^{3+} , Pr^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} CaF_2 : Na^{3+} , Ho^{3+} , Er^{3+} , Yb^{3+} , Sm^{2+} , Dy^{2+} , Tm^{2+} , U^{3+} SrF_2 : Na^{3+} , Tm^{3+} , Sm^{2+} , Dy^{2+} , U^{3+}

Table 1.1. (Continued)

4	Fluoride-Fluoride Mixed Fluoride	NaCaYF : Nd ³⁺ Ca ₂ Y ₅ F ₁₉ : Nd ³⁺ CaF ₂ -YF ₃ : Nd ³⁺ , Ho ³⁺ , Er ³⁺
5	Oxide-fluoride	Ca ₅ (Po ₄)F : Nd ³⁺ , Ho ³⁺
6	Oxide-sulphide	La ₂ O ₂ S : Nd ³⁺
7	Halides	LaCl ₃ : Pr ³⁺ LaBr ₃ : Pr ³⁺

materials. The first observation of stimulated emission has been made with self activated rare earth crystals PrCl_3 and PrBr_3 of 1 μm size in the year 1971 [77]. It quickly opened a new field of materials research. Subsequently synthesis and growth of several self activated laser materials have been reported. Scientists have searched for the new laser crystals as well as the way to improve the efficiency. Among the several new materials studied extensively, it was found that both phosphates and borates are promising materials for efficient stoichiometric lasers. A review on stoichiometric laser materials and their laser efficiencies has been presented by Danielmeyer [78].

1.7 SUMMARY

An outline of crystal growth from solutions has been made with an equal emphasis on both low and high temperature solution growth methods. Crystallisation kinetics such as nucleation, growth theories and various available growth techniques to grow better quality and large size crystals have been discussed briefly. Generally, laser crystals are being grown from melt. However, from the outline made on the growth of crystals from solution, it is obvious that an attempt to grow laser crystals is worth doing. Crystals with lesser thermal or mechanical defects than the melt grown crystals can be grown from the solution, because of reduction in growth temperature[79]. The major constraints in the solution grown crystals, incorporation of solvent ions and presence of inclusions can be minimised by selecting proper solvent and optimizing growth parameters respectively. The other problem namely size limitation is almost eliminated by adopting new techniques developed by combining more than one technique involved in the solution growth.