CHAPTER 1

INTRODUCTION TO SINGLE CRYSTAL GROWTH AND NANO CRYSTAL SYNTHESIS FOR SOLID STATE LASERS

1.1 SOLID STATE LASERS

Crystals play an important role for the development of industrial applications such as lasers, optoelectronics, superconductors, semiconductors, magnetism and piezoelectric transducers. Recently, crystalline and polycrystalline transparent materials are used in the preparation of solid state lasers (SSL). SSL are widely used in metal processing, medical applications namely eye surgery, red-green-blue (RGB) light sources in laser printers and projectors, environmental instrumentation measurements and optical transmission systems and nuclear fusion (Ikesue and Aung 2008). The birth and growth of laser crystal physics starts by the realization of the physical nature of stimulated emission in 1916 by Einstein. Townes and co-workers developed the ammonia microwave maser in 1954. Schawlow and Townes anticipated the possibility of designing an optical maser or laser in 1958. Realization of laser oscillation from solid state (Al\textsubscript{2}O\textsubscript{3}:Cr\textsuperscript{3+}) by Maiman (1960) paved the path for the development of large number of crystalline state lasing materials. Johnson and Nassau (1961) demonstrated the first continuous laser oscillation in Nd\textsuperscript{3+} doped CaWO\textsubscript{4} matrix. Which opens path for the new research areas in trivalent rare-earths (Nd\textsuperscript{3+}, Er\textsuperscript{3+}, Ho\textsuperscript{3+}, Ce\textsuperscript{3+}, Tm\textsuperscript{3+}, Pr\textsuperscript{3+}, Gd\textsuperscript{3+}, Eu\textsuperscript{3+} and Yb\textsuperscript{3+}), divalent rare-earth ions (Sm\textsuperscript{2+}, Dy\textsuperscript{2+} and
Tm$^{2+}$), transition metals (Cr$^{3+}$, Ni$^{2+}$, Co$^{2+}$, Ti$^{2+}$ and V$^{2+}$) and actinide ion U$^{3+}$ doped in various host materials (Koechner 1996).

1.2 CRYSTAL GROWTH OF MONOCLINIC DOUBLE TUNGSTATES

In recent days, crystalline lasers render a significant role in modern laser physics, nonlinear optics and quantum electronics. Optically pumped laser action has been demonstrated in many lasing ion activated crystal hosts covering a spectral region from visible to mid infrared. After the combination of semiconductor laser pumping source with the lasing crystals have led to a veritable revolution in solid state laser design. Crystal growth involves the phase transformation of material interest from solid, liquid and gaseous phase to well ordered solid phase. Report of Raman self conversion of lasing ions in double tungstate materials, followed by many researchers and lead to concentrate on the development double tungstate based lasers. Present investigation concentrates on the growth of potassium gadolinium double tungstate single crystals. In double tungstates, stimulated emission of Yb$^{3+}$ doped potassium based yttrium double tungstate single crystals were discovered by Kaminiskii et al (1971) and stimulated Raman self conversion of Nd$^{3+}$ doped KGd(WO$_4$)$_2$ was proposed by Andryunas et al (1985). Monoclinic double tungstates KRE(WO$_4$)$_2$ (RE=rare-earth) are interesting laser host materials for different application in solid state laser, waveguide laser and solid state lightings.

1.2.1 High Temperature Solution Growth

High temperature solution growth (HTSG) method categorises as liquid-solid equilibrium growth of single crystal and it was a commercially practiced process for single crystal growth. HTSG method has been used for several decades; the value of this method can be realized from the attempts for the growth of gem crystals. Remeika (1954) grew BaTiO$_3$ using KF as
solvent, later on numerous researchers have grown number of crystals from various fluxes for several applications. Elwell and Scheel (1975) have perceivably reviewed the historical perspective and modern development of HTSG method. This method can be used to grow the materials that

1. Melts incongruently or material decomposes before its melt
2. Sublimes before its melt or its vapour pressure is high at its melting point
3. Polymorphism occurs before reaching melting point
4. High melting point (growth experimentally impractical)
5. Suitable dopant incorporation (incompatible to matrix)

Desired materials are dissolved in the flux; which reduces the actual melting point or dissolved oxides and at supersaturation state crystal growth occurs at temperatures well below the normal melting point of the material. The solvents employed are either ionic salts or oxides or low temperature melting materials. Some common solvents used for flux method are KF, PbO, PbF₂, B₂O₃ and mixture of these. The growth can also be carried out using one or more constituents in excess amount and is termed as self flux technique. After the dissolution of desired material into the solvent at high temperature, supersaturation occurs by solvent evaporation or by cooling or by transport process (flow of solute from hotter to cooler region) for growth of the crystal. Quality of flux technique grown crystals depends on many conditions like, choice of suitable solvent, crystallization temperature, rate of cooling and crucible material (Laudise 1970). The ratio between solvent and solute plays a major role in the flux growth, which alters dissolution temperature, saturation point and viscosity of the solution. One major disadvantage of HTSG is the corrosive nature of the flux that limit the crucible selection and the frequent replacement of parts exposed to the corrosive vapour.
1.2.2 Choice of Flux

Though, large numbers of substances are crystallized with variety of flux material by HTSG method, it is limited to give generalized discussion for the ideal flux. From the literature, the most important factors to be considered in selecting a flux are

1. Flux solvent should not form solid solution with solute
2. Flux solvent should have relatively low temperature than the melting point of the solute
3. The flux solvent should have moderately large temperature dependent solubility
4. To prevent the incorporation of foreign ions, it is better to use common ion flux solvent
5. Less corrosive with growth container
6. Low viscosity (High viscous retracts the flow of solute particles)
7. Less vapour pressure
8. Solute must only be the stable solid phase at the flux solvent melt
9. Easy separation of solute without detrimental effect of flux

Selection of flux with all qualities mentioned is rare but a compromise can be made based on the type of crystal. In the present investigation, \( K_2WO_4 \) has been used as the flux solvent for the growth of monoclinic KGdW single crystals. Most commonly potassium based rare
earth double tungstates were grown using $K_2W_2O_7$ as flux. The crystals can be
grown with $K_2WO_4$ also. However, use of low viscous $K_2WO_4$ flux consumes
longer time compared with $K_2W_2O_7$, but the quality of the crystals grown with
$K_2WO_4$ flux possess better properties.

1.2.3 Top-Seeded Solution Growth

Top-seeded solution growth technique (TSSG) is the combination
of Czochralski and solution growth processes to grow crystals from high
temperature flux solutions. This technique was introduced by Linz and
described in detail by Belruss (1971). By TSSG method one can control the
parameters like, orientation, growth rate, perfection and doping in comparison
with spontaneous nucleation in ordinary flux growth method. Growth of
various materials is limited owing to slow growth rates. This type of seeded
growth needed more elaborate equipment than spontaneously nucleating flux
growth.

One can classify this method by three method of attaining supersaturation

1. Slow cooling growth in presence of seed crystal

2. Growth on the seed crystal in cool part of the gradient with excess solute in the hottest region

3. Growth on the seed by solvent evaporation

Growth procedure in slow cooling and solvent evaporation method
has advantages; there is no dissolving step and diffusion path which can be
shorter in some cases. Gradient cooling and solvent evaporation have
advantage that the crystal growth takes place isothermally. Due to
incongruent solvent volatilizes and variation in distribution constant, solvent evaporation method is not advisable for TSSG method. Thermal gradient process is one of the best methods for the growth of large crystals because the crystal size is not limited by the total amount of solute in the solvent. TSSG method consists of three major units (i.e.) crystal puller (translation and rotational assembly), high temperature furnaces and growth containers (crucibles).

1.2.3.1 Growth assembly

Aim of the present work is concentrated to grow KGd(WO$_4$)$_2$ single crystals by top-seeded solution growth method. An indigenously constructed resistive heating three zone furnace was employed for the growth. Kanthal A-1 heating element was used to wound around ceramic Al$_2$O$_3$ muffle. Maximum temperature range of this furnace is around 1200 °C; the required temperature is around 950 °C for KGdW growth using K$_2$WO$_4$ flux. K-type thermocouple was used to sense the temperature of the zones. Three temperature zones were controlled by programmed single loop Eurotherm temperature controllers separately. Seating arrangements were made up of alumina bricks and thick alumina cylinders. In order to avoid the heat radiation around the resistive wire wounded muffle, thermally insulated Zirconia fiber wool was filled up to 500 mm diameter up to an external steel cover. Top of the furnace was covered with two separate refractory bricks to prevent loss of heat; these alumina bricks consist of holes, which can be used to view the growth process without disturbing furnace profile. The schematic representation of the TSSG assembly is shown in Figure 1.1.
Figure 1.1 Schematic diagram of top seeded solution growth assembly

Axial temperature gradient profile was made to determine optimum region to place the crucible in the furnace. Temperature gradient profile of the resistive heating furnace is shown in the Figure 1.2. The axial gradient was important to grow KGdW single crystals using flux, which helps to generate convection flow inside the flux by the zones in the furnaces.
Figure 1.2 Temperature gradient profile of the resistive heating furnace

The mild steel made mechanical part of the assembly was attached with the main frame of the growth assembly and it has translational and rotational assembly to translate vertically and rotates the seed rod. Crystalline seed was directly attached with alumina seed holding rod using platinum wire. Selection of growth container is another important issue in HTSG method. It might have to withstand the temperature encountered in melting the materials and should not react with the materials. In this work, platinum crucible was used for the growth of KGdW single crystals using $K_2WO_4$ flux. It is compatible with the melting point and chemically inert with $K_2WO_4$ and KGdW and mechanically suitable with growth material.
1.3 TRANSPARENT CERAMIC LASERS

Transparent ceramics possess physical quality and superior optical property as compared with single crystalline materials. The novel laser materials possess some essential properties namely larger in size with high dopant concentration and controlled dopant distribution. High temperature grown single crystalline bulk crystals with constrains such as high temperature environment, sophisticated facilities and costly crucibles long time processes are used as lasing materials. Prolonged investigation on transparent ceramics technique invents a new class of materials with single crystalline nature for better laser oscillation. Continuous efforts have been put forward for the period of two decades to develop transparent ceramic laser as a significant material for high power laser oscillation. Translucent alumina ceramics were first proposed by Coble (1961), followed by various researchers with many kinds of translucent ceramics were reported for various industrial applications. Greskovich and Chernoch (1973) prepared Nd doped ThO$_2$-Y$_2$O$_3$ transparent ceramics with low efficiency pulsed laser oscillation. The first Nd:YAG transparent laser was developed and demonstrated with high efficiency laser oscillation by Ikesue et al (1995). Recently many transparent laser ceramics were reported for high power lasers.

1.3.1 Nano Powder Synthesis

To eliminate the complexity of single crystal growth, transparent ceramic materials were developed in recent years (Ikesue et al 2006). Nano crystalline precursors and novel sintering methods provide new dimension for the development of transparent ceramics (YAG and Y$_2$O$_3$). Reports on transparent ceramic materials are available only with cubic phase owing to its isotropy and uniaxial nature. In order to avail high transparency, researchers are dedicated towards cubic structured materials (Ikesue and Aung 2006).
is investigated in this present investigation. It is realized that highly oriented non-cubic crystalline materials can be obtained by strong magnetic field orientation technique (Braithwaite et al 1991). In this investigation, preparation of oriented nano crystalline non cubic KRE(WO$_4$)$_2$ (RE= Rare-earth) sub-micron particles was attempted.

It is understood that driving force required for densification in sintering process is proportional to the curvature of particle and inverse to its radius. Time taken for sintering the ceramics is decreased with decreasing particle size. Primary particles ranging between 10 and 100 nm are preferred. In addition, precursor powder should meet other requirements like controlled particle distribution, equiaxed shape, minimum degree of agglomeration, purity and controlled surface chemistry. Many preparation methods are reported for nano powder preparation such as co-precipitation, hydrothermal, spray-drying, sol-gel and combustion synthesis; among these sol-gel synthesizes have many advantages.

1.3.2 Sol-Gel Processing

Among the various methods for the synthesis of nanomaterials, sol-gel processing is considered as best method for preparation of high temperature materials (nano ceramic and glass) with relatively low temperature synthesis, simple equipments, phase uniformity and so on. In preparation of ceramic particles, metal alkoxides have been used as precursor, which undergoes catalyzed hydrolysis followed by condensation to form nano scale oxide and hydroxide particles. Alkoxide precursors hold disadvantages like, high felicity to the atmospheric moisture and uncontrolled alkoxide formation rate in multi-component nano ceramic system (Nishio et al 2000, Kodaira et al 2003). Metal salts overcome the above said difficulties and they are cheaper in cost, less complexity and easy going oxide formation.
Dissolution of metal salts along with chelating agent in a solvent results with metal complex.

### 1.3.2.1 Pechini sol-gel method

Pechini method is a simple method for synthesizing metal oxide powders in gel medium, whose starting materials are metal salts, citric acid and ethylene glycol under low temperature heat treatment (Pechini 1967). It allows the metal cations mixing at molecular level and the stoichiometric composition is achieved by chelating agent (Citric acid). Pechini method is also cost effective, yield homogenous composition, pristine and requires low calcination temperature. Recently nano materials that belong to phosphors and magnetic materials family were prepared by Pechini method.

Pechini method is based on polymerization of metal citrates using ethylene glycol as binder for chelation, hydrocarboxylic acid (polybasic acid) such as citric, tartaric and glycolic acids were used. On comparison, citric acid is widely exploited in this process, owing to its high chemical stability. Citric ligands coordinated metal complexes are more stable due to the strong coordination of citric ion (two carboxyl groups and one hydroxyl group) with the metal cation. Glycol is added for the formation of organic ester. Condensation reaction results in the liberation of water during the reaction and during heat treatment.

The essential steps of the polymerizable complex formation are presented in Figure 1.3. Metal salts are dissolved in appropriate solvent which is followed by the addition of excess citric acid, in order to achieve metal-citrate. Chelating agent and metal ions ratio play a crucial role in forming complete metal-citrate complex. Two molar ratios \([\text{CA}]/[\text{M}] = \text{CM}\) and \([\text{CA}]/[\text{EG}] = \text{CE}\), where [CA], [M], [EG] are moles of the complexing agent, moles of metal cations and moles of ethylene glycol, respectively. Resultant
CM describes the degree of chelation process and CE indicates the polymerization of the metal in the organic product. If CM < 1, precipitation of metals salts and non uniform chelation occurs as the result of insufficient chelating agents to chelate metal cations. For better chelation, CM must be greater than one and CE must be equal to one (Galceran 2007).

Figure 1.3  Flow chat of Pechini sol-gel synthesis process

The citrate and ethylene glycol solution is heated to 90 °C which results in rapid polymerization occurs. The continuous polymer layers are confirmed by the existence of two functional groups in the monomer, which allocates uniform distribution to metal cation. Plastic like gel is formed by the removal of superfluous liquid. Further increasing temperature results in the removal of un-reacted ethylene glycol. When the plastic like gel is dried for 130 °C, it produces the relatively hard material. Further heating the sample for 300 °C removes the organic components. The dried samples contain the
mixture of evenly distributed metal oxides. The crystalline end product is obtained by calcinating at 700 °C.

Citric acid is comparatively strong multifunctional organic acid in which the hydroxyl group attach with ternary carbon atom and it enhances the acidity of middle carboxylic group (\(-^m\text{COOH}\)). Citric acid is well soluble in ethylene glycol and chemical interaction between citric acid and ethylene glycol occurs at room temperature without any treatment of the solution. This interaction is not complete and in chemical equilibrium. Destabilizing effect provided by two methylene groups is reduced by the neighbouring terminal of carboxylic groups (\(-^{t}\text{COOH}\)), by which middle carboxylic group very easily loses H\(^+\) in water (Harris 1976). pH of the solution plays a crucial role in the function of citric acid. When the pH is 0-2, the nature of citric acid remains same. When pH approaches neutral value, all the \(-\text{OH}\) groups are protonated and removal of H\(^+\) occurs. It is reasoned that terminal carboxylic groups dissociates at moderate pH (Grigor’eva 1975). Location of this middle \(-\text{OH}\) group is favourable for the formation of hydrogen bonds between carboxylic groups and hydroxyl group, such a skeleton is responsible for the formation of stable rings in metal citrate complexes.

1.4 AIM AND SCOPE OF THE THESIS

The present investigation deals with the growth of 0.5, 2 and 5wt% \(\text{Pr}^{3+}\) doped KGd(WO\(_4\))\(_2\) (KGDW) using TSSG technique. And the powder synthesis of pure and doped KRE(WO\(_4\))\(_2\) (RE=Ln\(^{3+}\)) using Pechini polymeric mixed-metal precursor sol-gel method.

Various concentration of \(\text{Pr}^{3+}\) doped KGDW crystals were grown with low viscous K\(_2\)WO\(_4\) flux system using TSSG method. The crystals were characterized using analytical methods. The effect of concentration of \(\text{Pr}^{3+}\) ions in the KGDW matrix was discussed with single crystal XRD results.
Concentration dependent quenching of de-excitation transition of $^1\text{D}_2$ of Pr$^{3+}$ ions were discussed with absorption and emission spectral analysis. Formation of tungstate double bridge was confirmed and the dopant effect on KGdW matrix was discussed with Raman spectra.

Effect of pH (3.5, 5.5 and 7.5 pH) on sol-gel synthesised monoclinic KGdW crystalline powders and their magnetic texturing effect were discussed in detail. Nature of gel and calcination effect on different pH derived gel at high temperature was detailed with powder XRD and FT-IR analysis. Variations in the topographical properties of the synthesised powder with respect to pH and calcination sources were discussed.

Investigation on synthesis of nano crystalline KHo(WO$_4$)$_2$ (KHoW) at 3.5 pH and influence of calcination temperatures on morphology, optical and magnetic measurements were discussed for derived KHoW powders. Thermal analysis and FT-IR analysis enumerated the nature of degradation of the derived gel. Enhancement of crystallinity and tungsten double bridge formation at higher calcination temperature is discussed via powder X-ray diffraction pattern and Raman analysis. Nano particle formation and morphological changes with increasing calcination temperatures were explained with TEM and FE-SEM analysis. The absorption and emission studies were correlated with application of nano KHoW powders for laser devices and magnetization effect was discussed through VSM of KHoW.

The effect of Bi$^{3+}$ sensitization and high CTB MoO$_4^{2-}$ dopant on the luminescence properties of sol gel derived Eu$^{3+}$:KGdW nano crystals were investigated. Synthesis of hybrid nano composite Eu$^{3+}$ doped KGdW capped SiO$_2$ nano spheres was also analyzed. Effect of dopant in the KGdW matrix was investigated with Raman analysis and luminescence properties of KGdW doped with different concentration of dopants was compared. Preparation of
silica coated with Eu\textsuperscript{3+} doped KGdW using sol-gel technique was explained, their structural and optical characterization properties were discussed.

The stoichiometric replacement of Gd\textsuperscript{3+} by different lanthanides from La\textsuperscript{3+} to Lu\textsuperscript{3+} in KGdW matrix was attempted via sol-gel technique and their structural, morphological and magnetic changes were attributed using powder XRD, Raman, FE-SEM, VSM, zero field cooling (ZFC) and field cooling (FC) magnetization measurements, respectively. Detailed results on different material systems are summarized and suggestions for future work are proposed.