CHAPTER 2

GROWTH OF POTASSIUM GADOLINIUM TUNGSTATE SINGLE CRYSTALS AND THEIR CHARACTERIZATION

2.1 INTRODUCTION

Stimulated emission properties of potassium gadolinium tungstate KGd(WO₄)₂ single crystal doped with rare earth ions were discovered in 1971 (Kaminskii et al 1971). The low temperature phase of KGd(WO₄)₂ (KGW) single crystals, have a monoclinic structure and belongs to the C2/c space group. This crystal structure of tungstate enables active ions to be introduced and makes these crystals to be employed as laser host materials. Their thermal, optical and mechanical properties make them suitable for solid state laser applications. Presence of large third order nonlinear susceptibilities in these monoclinic tungstates extend its application in various laser experiments and application based on Stimulated Raman Scattering (SRS) phenomenon (Grabtchikov et al 2000).

Potassium gadolinium tungstate (KGW) undergoes a polymorphic structural transformation at 1005 °C. Therefore, the monoclinic α-KGW cannot be grown from stoichiometric melt using conventional Czochralski technique (Brenier et al 2001). However, the crystal growth is possible from high-temperature solution growth at a temperature below the polymorphic structural phase transition temperature. Solution based techniques were attempted to grow bulk KGW single crystals. Top-seeded solution growth (TSSG) (Guofu Wang et al 1990), induced nucleated floating crystal (INFC) growth (Metrat et al 1999) and vertical Bridgman-Stockbarger method (Gallucci et al 2000) are some of the solution growth techniques successfully
used to grow tungstates. TSSG is the most important and widely used method for the growth of device quality KGW single crystals. It is often called modified Czochralski method, because the only difference from the conventional Czochralski method is that utilization of an appropriate flux or a solvent instead of pure or stoichiometric melt. The pure KGW single crystals were grown by TSSG technique with the help of $\text{K}_2\text{WO}_4$ and $\text{K}_2\text{W}_2\text{O}_7$ solvents. The growth parameters were optimized. The grown crystals were characterized to find the suitability of the material for solid state laser applications.

2.2 PROPERTIES OF POTASSIUM GADOLINIUM TUNGSTATE

Extensive studies were made on KGd(WO$_4$)$_2$ single crystals and their evaluations of physical, chemical, optical and mechanical properties. Potassium gadolinium tungstate crystallizes in two different structures. The high temperature phase is a tetragonal structure which is not suitable for device application (Gallucci et al 2000 and Pujol et al 2001). The other phase is monoclinic structure, which crystallizes at low temperature. Important properties of monoclinic KGW crystal are given in the Table 2.1 (Musset et al 1997 and Pujol et al 2001).

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Monoclinic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>C2/c</td>
</tr>
<tr>
<td>Lattice parameters</td>
<td>$a=10.65\text{Å}$, $b=10.37\text{Å}$, $c=7.58\text{Å}$, $\alpha=\gamma=90^\circ$, $\beta=130.80^\circ$ and $V=634\text{Å}^3$</td>
</tr>
<tr>
<td>Density</td>
<td>7.27 g/cm$^3$</td>
</tr>
<tr>
<td>Moh’s hardness</td>
<td>5 Mho</td>
</tr>
<tr>
<td>Transmission range</td>
<td>0.34- 5.5 $\mu$m</td>
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<tr>
<td>Refractive indices @ 1.067$\mu$m</td>
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</tr>
<tr>
<td>Melting temperature</td>
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</tr>
<tr>
<td>Phase transition temperature</td>
<td>1005 °C</td>
</tr>
<tr>
<td>Thermal Conductivity Wm$^{-1}$K$^{-1}$</td>
<td>2.6</td>
</tr>
</tbody>
</table>
2.3 SYNTHESIS OF KGd (WO₄)₂ PRECURSORS

Chemical synthesis of the KGW charge was carried out with the basic chemicals such as Potassium Carbonate (K₂CO₃), Gadolinium oxide (Gd₂O₃), and Tungsten oxide (WO₃). The purity of the chemicals used were more than 99.9 % to avoid segregation and incorporation of impurities in the crystals.

The non-stoichiometric composition of K₂CO₃, Gd₂O₃ and WO₃ in 3:1:6 ratio was taken for the synthesis. So that the synthesized charge contains both KGd(WO₄)₂ and the flux K₂WO₄ in predetermined composition liberating CO₂ as per the solid state chemical reaction given by

3 K₂CO₃ + Gd₂O₃ + 6WO₃ \rightarrow 2KGd(WO₄)₂ + 2K₂WO₄ + 3CO₂

Similarly the composition of K₂CO₃, Gd₂O₃ and WO₃ was taken as 3:1:8 during the synthesis for the flux K₂W₂O₇.

3 K₂CO₃ + Gd₂O₃ + 8WO₃ \rightarrow 2KGd(WO₄)₂ + 2K₂W₂O₇ + 3CO₂

The known compositions of the chemicals were mixed and the mixtures were taken in a platinum crucible and kept in the resistive heating furnace. The furnace temperature was raised to 800 ºC at a heating rate of 50 ºC/h and maintained at the same temperature for 10 hours to get the solid-state reaction. Then the furnace temperature was cooled to room temperature at the rate of 30 ºC/h. At the end of the synthesized process, the CO₂ was completely removed from the charge. The synthesized charge was transferred to a mortar from the platinum crucible and was crushed for some time to have homogeneous powder. The composition of the homogenized powder was
confirmed from the powder XRD and IR spectrum analyses. Then the powder charge was utilized for crystal growth.

2.4 PREPARATION OF SEED CRYSTALS BY SPONTANEOUS NUCLEATION

Seed crystals of KGW were prepared by spontaneous nucleation induced by slow cooling method. The synthesized charge was filled in a platinum crucible of volume 30 cc and melted in a home made three zone resistive heating furnace. The furnace temperature was controlled and monitored by the Eurotherm 2604 model multi loop PID temperature controller. K-type thermocouple was employed. The temperature profile was adjusted in such a way to keep the crucible bottom at a higher temperature. This will avoid the crystallization at the bottom of the crucible during the growth.

During the growth run, the charge was filled in the crucible and was placed inside the furnace and the temperature was slowly raised above the melting point of the material. After completely melting the material, the molten solution was kept at the same temperature for one day to get a homogenized solution. Then the temperature was reduced very slowly at the rate of 0.1-0.3 °C/h to find the supersaturated state. (If the liquid phase is supersaturated with respect to the state of equilibrium but the solid phase is absent, the system is metastable. The formation of nucleation is favorable if there is further reduction in the temperature). After attaining the supersaturated state; the temperature was reduced very slowly to form the nucleus. The formation of nucleus is a very important stage, when their dimensions overcome some critical value, they are able to grow spontaneously. These growth experiments will yield polycrystals during the early stage of the growth process. By trial and error method, the growth
conditions were optimized. The cooling rate of 0.1°C/h resulted in better quality crystals. After optimizing the growth conditions single crystals of dimension 1 x 0.5 x 0.5 cm³ were obtained.

Figure 2.1 (a) As grown & (b) Polished seed crystals obtained by flux method
By polishing the harvested crystal, seeds were prepared in different size and shape as shown in Figure 2.1. Opaque part of the seed indicates that the grown crystal has flux inclusions. Inclusion free crystals were grown by top seeded solution growth method (Senthil Kumaran et al 2005a), using seed crystals obtained by slow cooling technique.

2.5 GROWTH OF PURE KGW CRYSTALS BY TOP SEEDED SOLUTION GROWTH

Pure potassium gadolinium tungstate KGd(WO$_4$)$_2$ single crystals were successfully grown by top seeded solution growth technique. Growth parameters were optimized with different flux systems to get inclusions free device quality crystals. Top seeded solution growth is a technique, in which crystals can be grown at the surface of the solution by introducing the seed when the temperature at the surface is lower than at the bottom of the solution. During the growth, the crucible was placed inside the furnace having a desirable axial temperature gradient. The temperature was raised to melt the charge in the crucible. The molten solution was kept at the same temperature for 24 hours to get a homogenized melt. The crystal harvested from spontaneous nucleation technique was employed as seed for the growth process. One end of the alumina rod was attached to the rotation cum translational unit. A platinum foil of thickness of 0.5 mm was attached to another end of seed rod (alumina). The seed crystal was tightened at free end of platinum foil using platinum thin wire. Thus the seed was mounted in the alumina rod of 6 mm diameter with a centre hole of 1 mm diameter. The seed was then dipped in the unsaturated molten solution and was continuously monitored to confirm that it had started dissolving. Then the solution was slowly cooled and the seeding was repeated simultaneously, to find the exact value of temperature for super saturation of the solution.
After knowing the exact super saturation temperature, seeding was carried out. The seeding was continuously monitored for the initiation of the growth on the seed. Once the growth had started in the seed, cooling and pulling process were made simultaneously at the rate of 0.1 °C/hr and 0.04 mm/hr respectively. Increase in the cooling rate or the pulling rate seemed to affect the quality of the crystal with undesirable inclusions. The rotation of the seed was kept constant at 20 rpm to maintain the homogeneity of the solution and a constant growth rate. After the growth was over, the grown crystal was detached from the molten solution and the furnace was cooled at 20° C/h to the room temperature in order to avoid the thermal shocks. The photograph of the furnace and crystal puller employed for the present work is shown in Figure 2.2.

Figure 2.2  Photograph of the crystal puller with the high temperature furnace.
As grown, cut and polished single crystals of potassium gadolinium tungstate are shown in Figure 2.3.

Figure 2.3  (a) As grown (b) cut and polished pure K\text{Gd(WO}_4\text{)}_2 single crystals
2.5.1 Role of Flux

Flux or solvent plays a vital role in the growth of pure KGd(WO$_4$)$_2$ single crystals by TSSG. Since this component exhibits polymorphic phase transition below its melting point, two different flux systems namely K$_2$WO$_4$ and K$_2$W$_2$O$_7$ were employed. Suitable flux system for the growth of pure KGW single crystals was identified by keeping the growth parameters, flux and solute ratio as constant (45% solute and 55% solvent) values. Growth runs were carried with K$_2$WO$_4$ and K$_2$W$_2$O$_7$ flux systems. The crystals obtained using the flux systems (K$_2$WO$_4$ and K$_2$W$_2$O$_7$) do not indicate any difference in properties or in quality. The saturation temperature is lower when the K$_2$W$_2$O$_7$ flux system was used since the melting point of the K$_2$W$_2$O$_7$ flux is 619 °C. This is about 270 °C lower than that of the K$_2$WO$_4$ flux (Manuilov et al 1999 and Sole et al 1996). However, larger crystals were obtained from K$_2$WO$_4$ flux compared with the K$_2$W$_2$O$_7$ flux system for the identical conditions of the growth procedure. The reason behind, is that their growth rate is inversely proportional to the viscosity of the mixture (Gallucci et al 2000). The excess tungstate present in the K$_2$W$_2$O$_7$ will increase the viscosity of the molten solution. High viscous may lead to a slower growth rate. It is concluded that the K$_2$WO$_4$ appears to be a suitable solvent for the growth of monoclinic structured KGW single crystals. The pure KGW crystal is colorless and highly transparent (Senthil kumaran et al 2005a).

2.5.2 Conditions for Inclusion Free Crystals

Efforts were made to explore the ideal growth parameters to get inclusion free single crystals. The main criteria being the seeding temperature, which was measured by trial and error basis. Then inclusion free seed was immersed at few degrees above the saturation temperature so that the outer surface of the seed got dissolved into the solution. Then the temperature was
decreased slowly till the exact saturation temperature is reached. Growth was initiated after attaining the saturation. During the growth process, seed rotation and translation was kept at 20 – 30 rpm and 0.5 mm/day of pulling respectively. The cooling rate was maintained at 0.1- 0.3 °C/h. The saturation temperature lies between 940 – 980 °C and 900 – 930 °C for K₂WO₄ and K₂W₂O₇ fluxes respectively (Senthil kumaran et al 2005a).

The preparation and growth of pure KGd(WO₄)₂ pose some difficulties. The existence of the high temperature polymorphic phase transition below its melting point, prohibits the growth of these materials by conventional melt process. The loss of tungsten trioxide due to its volatility (Gallucci et al 1998) creates non-stoichiometry in the melt. The polyphased fiber deposition of tungsten trioxide on the ceramic seed rod during the growth of KGW single crystal was shown in Figure 2.4(a). During flux growth of these materials, the tungsten trioxide evaporation was a major problem since the growth period is long (around 15 days). This will affect the quality as well as the stoichiometry of the growing crystal. The solute and flux ratio was optimized to compensate the loss of tungsten trioxide and 35 – 45 % flux and 55 – 65% solute ratio produced comparatively good results.

Figure 2.4 (a) Polyphased fiber deposition on the seed rod
Multi-nucleation on seeding is another problem during the growth of KGW. The formation of multi nuclei during the growth was illustrated in Figure 2.4 (b). Multinucleation was partly avoided by optimizing the rotation rate and the temperature gradient.

![Multi nuclei formation on the surface of the melt](image)

**Figure 2.4 (b) Multi nuclei formation on the surface of the melt**

### 2.6 CHARACTERIZATION STUDIES ON KGD(WO₄)₂ SINGLE CRYSTAL

Characterization studies are an integral part of crystal growth, since most of the physical properties of the crystals are sensitive to the growth parameters and the growth technique, which are employed for the growth of crystals. In general, the crystals grown by different techniques contain some defects, impurities and inhomogeneity. Therefore it is essential to correlate the quality of the crystal with the growth technique and the growth parameters. Hence, systematic characterization results enable to optimize the growth parameters in order to obtain better quality crystals. The grown crystals were cut and polished. Different characterization studies, such as Powder X-ray diffraction (XRD), Differential Thermal Analysis (DTA), IR and Raman spectroscopic analysis, Optical transmission and absorption analysis were carried out on the grown crystals.
2.6.1 Differential Thermal Analysis (DTA)

In a differential thermal analysis (DTA) involves heating or cooling a test sample and an inert reference under identical conditions, while recording the temperature difference between the sample and reference. This differential temperature is then plotted against time or against temperature. Changes in the sample which leads to the absorption or evolution of heat can be detected relative to the inert reference. Differential temperatures can also rise between two inert samples when their response to the applied heat treatment is not identical. DTA can therefore be used to study thermal properties and phase changes in the test sample.

Differential thermal analysis (DTA) for pure KGW was performed using STA 409 apparatus. Powdered sample of about 130 mg was used in open platinum pans and heated from 300 °C to 1200 °C. The heating rate was 5 deg/min in argon atmosphere. DTA curve obtained for pure KGd(WO$_4$)$_2$ is shown in Figure 2.5 Two strong endothermic peaks were detected at 1030 °C and 1087 °C, which are attributed to the polymorphic phase transition and melting point of the material respectively.
2.6.2 Powder X-Ray Diffraction Analysis

Powder X-ray diffraction is an efficient analytical technique used to identify the fine structure of crystalline materials. Samples are analyzed as powders with grains in random orientation to insure that all crystallographic directions are sampled by the beam. When the Bragg’s conditions for constructive interference are obtained, a reflection is produced, and the relative peak height is generally proportional to the number of grains in a preferred orientation. The X-ray spectra generated by this technique, thus, provide a structural fingerprint of the unknown mixtures of crystalline materials and relative peak heights of multiple materials may be used to obtain semi-quantitative estimates of abundances.

The monoclinic structure of pure KGW crystal was confirmed by powder X-ray diffraction analysis. The XRD analysis was carried out for the powder sample using RIGAKU RINT 2000 model x-ray diffractometer. X ray source is Cu-K-\(\alpha\) radiation operated at 40 kV/30mA and wavelength of 1.5418 Å. The diffraction pattern confirms (Figure 2.6) that the grown crystals are monoclinic with a space group of C2/c.

Figure 2.6 Powder XRD spectrum for pure KGW crystal
The lattice parameters were calculated from the single crystal X-ray diffraction analysis. The values are \(a = 10.64\ \text{Å}, b = 10.43\ \text{Å} \) and \(c = 7.58\ \text{Å}, \alpha = 90^\circ, \beta = 130.73^\circ \) and \(\gamma = 90^\circ\) and \(V = 638\ \text{Å}^3\). The values obtained from the single crystal XRD analysis are in good agreement with the literature values (Pujol et al 2001).

### 2.6.3 Optical Absorption

The absorption of radiant energy in the visible and ultra violet spectral regions depends primarily on the number and arrangement of the electrons in the absorbing molecules or ions. Therefore absorption is a property of a particular sample and will vary with the concentration of substance present in the test sample and the thickness of the sample material.

Among inorganic substances, selective absorption may be expected whenever an unfilled electronic energy level is covered or protected by a completed energy level, usually formed by means of coordinate covalence with other atoms.

Experimental measurements are usually made in terms of transmittance (T), which is defined as the light intensity after it passes through the sample over the initial light intensity. Modern spectrometers can usually display the data as either transmittance, or absorbance. Absorbance is the negative logarithm of transmittance.

The optical absorption measurements at room temperature were carried out for pure KGW single crystals. The samples (1-2mm thick) were prepared from the as grown pure KGW boule. Figure 2.7 shows the absorption spectrum for pure KGW. There was no absorption peaks and the
cut-off wavelength at the UV band edge was around 332 nm. This cut-off value may be due to Gd-O electronic transition (Sole et al 1996).

Figure 2.7 Absorption spectrum for pure KGW

2.6.4 IR Spectrum Analysis

Fourier Transform Infrared spectroscopy (FTIR) is a powerful tool for identifying the types of chemical bonds present in a molecule by producing an infrared absorption spectrum that is like a molecular "fingerprint". FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantify some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gases. The term Fourier Transform Infrared Spectroscopy (FTIR) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum.

The absorption of infrared radiation depends on increasing the energy of vibration or rotation associated with a covalent bond, provided that
such an increase results in a change in the dipole moment of the molecule. This means that nearly all molecules containing covalent bonds will show some degree of selective absorption in the infrared.

IR spectrum for pure KGW single crystals were recorded in the range from 500 cm\(^{-1}\) and 4000 cm\(^{-1}\) and is shown in Figure 2.8. The bands between 500 cm\(^{-1}\) and 1000 cm\(^{-1}\) may be attributed to the symmetric vibrations of tungstate ion and W-O-W bridge band vibrations. The region between 1000-2000 cm\(^{-1}\) may be due to a complex multiple of second-order vibrational transitions like tungsten-Oxygen stretch, two level combinations of stretching and bending modes (Macalik et al 1998). The peaks between 2000 – 3000 cm\(^{-1}\) corresponding to impurities like H\(_2\)O and CO\(_2\) stretching which are absorbed as traces.

![Figure 2.8 IR spectrum for pure KGW](image-url)
2.6.5 Raman Spectra Analysis

In Raman spectroscopy, a molecule is exposed to a light beam and scattered light are obtained at a higher or lower energy due to the exchange of energy with the molecule, leaving the molecule in a lower or higher vibrational state. Deflected or scattered light with higher frequencies is referred to as anti-stokes scattering, and with lower frequencies as stokes scattering.

A Raman spectrum is a plot of the intensity of Raman scattered radiation as a function of its frequency difference from the incident radiation (usually in units of wavenumber, cm\(^{-1}\)). This difference is called the Raman shift (The Raman shift is independent of the frequency of the incident radiation).

A laser is used to excite Raman spectra because it gives a coherent beam of monochromatic light. This gives sufficient intensity to produce a useful amount of Raman scatter and allows for clean spectra, free of extraneous bands. Laser used for Raman spectroscopy must exhibit good wavelength stability and low background emission. Raman spectra originate in the electronic polarization caused by ultraviolet or visible light. If molecules are irradiated by a monochromatic light of frequency \(\nu\), then, because of electronic polarization induced in the molecule by this incident light, light of frequency \(\nu\) (rayleigh scattering) as well as \(\nu \pm \nu_i\) (Raman scattering) is emitted (\(\nu_i\) represents vibrational frequency). Thus the vibrational frequencies are observed as Raman shifts from the incident frequency \(\nu\) in the ultraviolet or visible region.

Raman spectra for pure KGW were recorded in the back-scattering configuration using Ar 488 nm line and are shown in Figure 2.9. Prominent
Raman lines (intense) are observed at 904 cm$^{-1}$ and at 763 cm$^{-1}$. Raman line at 904 cm$^{-1}$ corresponds to the asymmetric stretching vibration of W-O-W bridge band (Macalik et al 1998). These two strong peaks make KGW more attractive for Stimulated Raman Scattering (SRS) applications due to their large cross section. In addition to these prominent lines, several lines are observed in the region 450-700 cm$^{-1}$ which may be attributed to the oxygen bridge band W-O-W and W-O-O-W vibration. The bridge band modes play an important role in the electron-phonon coupling and consequently in the energy transfer in these crystals (Hanuza et al 1994).

Figure 2.9 Raman spectra for pure KGW
2.7 COMPARISON OF RESULTS FROM DIFFERENT REPORTS FOR KGd(WO₄)₂

<table>
<thead>
<tr>
<th>Properties</th>
<th>Results from different reports</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Guo et al</td>
</tr>
<tr>
<td>Growth Technique</td>
<td>TSSG</td>
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<tr>
<td>Solvent</td>
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<td>Phase Transition</td>
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<td>Stimulated Raman Scattering Active modes</td>
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</tr>
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<td>Optical Transparency</td>
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</tr>
</tbody>
</table>

2.8 SUMMARY

Potassium gadolinium tungstate KGd(WO₄)₂ seed crystals were prepared by slow cooling technique. With the help of a seed, device quality large size single crystals of pure KGd(WO₄)₂ were grown by top seeded solution growth technique. Growth conditions were optimized for different flux systems namely K₂WO₄ and K₂W₂O₇. The saturation temperature lies between 940 – 980 °C and 900 – 930 °C for K₂WO₄ and K₂W₂O₇ respectively. Monoclinic structure of grown crystal was confirmed by powder XRD analysis and the lattice parameters were calculated from the single crystal XRD analysis. Differential thermal analysis shows that the KGW single crystal exhibits polymorphic phase transition around 1030 °C and it completely melts at around 1087 °C. Optical absorption spectrum shows the cut-off wavelength at the UV bandedge at around 332 nm. This cut-off value may be due to Gd-O electronic transition. Raman spectrum reveals a prominent line located at 904 cm⁻¹ with the possibility of strong emission during SRS.