ABSTRACT

From the beginning, the uses of solid state laser in the field of science and technology had increased rapidly. Present scenario needs laser host materials emitting wide spectral for variety of applications. Therefore, in recent years, considerable interest was generated for the development of laser host materials with enhanced non-linear optical (NLO) properties; hence the materials with different orders of nonlinearities generate lasing with multiple frequencies.

The existence of high laser efficiency, low laser induced damage threshold and high third-order nonlinear effect has received a lot of attention on the growth of alkali- metal based double tungstate single crystals for novel solid state lasers. In particular, potassium gadolinium tungstate KGd(WO$_4$)$_2$ (hereafter KGW) and potassium yttrium tungstate KY(WO$_4$)$_2$ (hereafter KYW) single crystals doped with rare-earth ions are promising materials. These tungstates are highly efficient Raman media due to the structure symmetry connected with the vibration symmetry of molecular WO$_4^{2-}$ group. KGW and KYW have a tetragonal structure when crystallized from the melt. The monoclinic phase (α) called low temperature phase appears below its melting point. This monoclinic structure is very useful in variety of applications.

The present study enumerates the growth aspects of pure KGd(WO$_4$)$_2$, Nd: KGd(WO$_4$)$_2$, Yb:KG(WO$_4$)$_2$, Pure KY (WO$_4$)$_2$ and Nd:KY (WO$_4$)$_2$ by high temperature top seeded solution growth technique. Two flux systems namely K$_2$WO$_4$ and K$_2$W$_2$O$_7$ were used for the growth of KGW and KYW pure and doped single crystals. Two rare earth ions - Nd$^{3+}$ and Yb$^{3+}$ were used for the
present work. Crystals were grown with different molar concentration of rare earth ions (Nd$^{3+}$, Yb$^{3+}$). The thesis is categorized into five chapters.

Pure potassium gadolinium tungstate KGd(WO$_4$)$_2$ seed crystals were prepared by flux technique. With the help of the seed, device quality large size single crystals of KGd(WO$_4$)$_2$ were grown by top-seeded solution growth technique. Growth conditions were optimized for different flux systems namely K$_2$WO$_4$ and K$_2$W$_2$O$_7$. The role of flux and the optimum ratio between the flux and the solute were investigated. The saturation temperature lies between 940 – 980 °C and 900 – 930 °C for K$_2$WO$_4$ and K$_2$W$_2$O$_7$ 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 the KGW single crystal having a polymorphic phase transition at around 1030 °C and completely melting at around 1087 °C. Optical absorption spectrum shows the cut-off wavelength at the UV bandedge around 332 nm. This cut-off value may be due to the Gd-O electronic transition. Raman spectrum reveals a prominent line located at 904 cm$^{-1}$ with the possibility of strong emission during SRS.

Good quality Nd$^{3+}$ and Yb$^{3+}$ doped KGd(WO$_4$)$_2$ single crystals were grown by top-seeded solution growth technique. Growth parameters were optimized for the growth of inclusion free crystals suitable for the solid state laser applications. From the as grown boules of Nd: KGW and Yb: KGW, the crystal samples were prepared and subjected to different characterization studies to get the physical, chemical, mechanical and optical data. Powder XRD spectra confirms that the grown crystals are monoclinic in structure and doping incorporation (1-3% of Nd or Yb) has not altered the lattice parameter to a considerable extent. It was also confirmed from the single crystal XRD data. Electron probe micro analysis (EPMA) was done for Nd$^{3+}$ doped KGW
sample to acquire the doping concentration over the sample. It shows the uniform doping distribution of rare earth ions which is essential for laser application. 2 mm x 2 mm size sample was employed for EPMA analysis. Analyses were carried out on different spots. The result shows that Nd\(^{3+}\) distribution is uniform throughout the sample.

UV-Vis spectra indicates that Nd\(^{3+}\): KGW has cut-off wavelength same as pure KGW. Well-defined absorption bands are centered at 354 nm in the ultraviolet regions, at 532 nm and 581 nm in the visible region and at 753 nm and 811 nm in the near infrared region respectively. The absorption band at 811 nm is more intense and can be used for diode laser pumping to have compact diode pumped solid state lasers. For Yb\(^{3+}\): KGW single crystal the absorption peak is centered at around 980 nm.

Laser element was prepared from 3% Nd doped KGW single crystal and the emission studies were carried out with the help of second harmonic pulsed Nd: YAG laser (532 nm and 10 mJ). Pumping was done at 532 nm absorption peak. The result shows the Nd: KGW having lasing at around 1069 nm. This band corresponds to the \(4\)\(^{2}F_{3/2} - \)\(^{4}I_{11/2}\) lasing channel of Nd ions.

Stimulated Raman Scattering measurements were made on a 2 mm thick Yb: KGW crystal sample. Pulsed second harmonic Nd: YAG laser was used as the pumping source with energy 10 mJ. The additional Raman lines were observed besides the pumping wavelength of 532 nm. The Stokes lines were observed at 585 nm, 556 nm and at 617 nm. There are no anti-Stokes lines as the pumping energy was very low. The result indicates that the rare earth doped KGW single crystal can be used for multi-frequency laser applications.
Potassium yttrium tungstate KY(WO₄)₂ pure and Nd³⁺ doped single crystals were grown with the help of K₂WO₄ solvent. The growth parameters were optimized to get the device quality bulk crystals. The grown crystals were cut and polished and the samples were subjected to structural, mechanical and optical characterization. Powder and single crystal XRD analyses confirm that the grown crystals are monoclinic in structure and the lattice parameters are in good agreement with the literature values. The calculated values are a = 10.64 Å, b = 10.32 Å, c = 7.55 Å and α = 90°, β = 130.31°, γ = 90°, and V = 633Å³. Micro hardness studies indicate that the hardness value increases as the load increased. IR and Raman study confirms that all the vibrational modes are present in the crystal. Two strong peaks observed at 763 cm⁻¹ and 904 cm⁻¹ makes KYW more attractive for Stimulated Raman Scattering (SRS) applications due to their large cross-section. The lines observed in the region 450 cm⁻¹ to 700 cm⁻¹ correspond to the oxygen bridge bond WOW and WOOOW vibration. Raman spectra observed for the pure and doped KYW indicates no significant changes in the assignments, but the intensities of lines weaken and broaden due to the doping of Nd³⁺ ions. The intense Raman line at 904 cm⁻¹ is most interesting for third order non-linear applications and this line corresponds to the symmetric stretching of the W polyhedron. Finally, the summary of the present investigation and the suggestions for the future work were explained in detail.