

SUMMARY AND CONCLUSIONS

In my thesis I have studied the effect of preparation procedure and growth parameters on the properties of three materials (i) CsI and (ii) $\text{NaR}(\text{WO}_4)_2$; $\text{R} = \text{Gd, Bi}$ as a prompt scintillator in the form of single crystals and (iii) Mn doped CaF_2 (in the form of OTC) as a material for thermally stimulated luminescent dosimeter. The aim of the study was to make single crystal growth procedure easy and simple and second, to develop a better substitute for Mn doped CaF_2 single crystals for applications in radiation dosimetry.

Tl doped CsI single crystal: Single crystals of CsI are conventionally grown using the Bridgman technique. The growth of CsI crystals does not pose major problems. However, sticking of the grown crystal to crucible walls makes their extraction difficult and stresses are generated during the recovery process. These issues are important and need to be addressed to grow device grade crystals. In this Ph.D. work two different approaches were opted to grow detector grade single crystals of Tl doped CsI of 50 mm diameter and 60 mm length; (i) Growth of CsI:Tl single crystals in carbon coated silica crucibles and (ii) Growth of CsI:Tl crystals using a modified Bridgman method.

In the first method, single crystal of Tl doped CsI crystals of 35 mm diameter and 40-50 mm length were grown in carbon coated fused silica crucibles by a gradient freeze technique that exhibited good radiation hardness. Effects of the axial temperature gradient inside the melt, cooling rate and post-growth annealing on the crystal growth and luminescence properties have

been studied and optimum conditions were found. Results of a systematic study carried out on the effects of growth process on radiation hardness, day-light coloration and related afterglow of CsI:Tl was studied. A possible process of defect formation for induced coloration is proposed and methodology adopted for their successful removal is discussed.

In a different approach a modified Bridgman technique was developed to grow the CsI single crystal of 50-55 mm diameter and 60-70 mm length. The Bridgman furnace, employed for crystal growth, consists of four independently controlled resistive heating elements. Top isothermal zone consisting two heating element is separated from bottom isothermal zone using a 50 mm thick baffle (adiabatic zone). A maximum 20°C/cm temperature gradient was achieved in the adiabatic zone. A specially designed silica glass crucible was used for the growth. The main advantage of the process was that the grown crystal was not in the contact of the crucible wall during annealing and cooling. Scintillation performance of the crystals grown by these two methods were tested and found excellent. Other alkali halide crystals like NaI, NaCl, KBr etc have also been grown successfully employing this technique.

In summary a cost effective Bridgman single crystal growth system has been developed which can be used to grow high quality halide single crystals (NaI, CsI, KBr etc.). By employing this technique the thermal and mechanical shocks to the crystal were avoided that minimized the day light coloration and enhanced the radiation hardness of the grown crystals. The developed technology is ready to be transferred to small-scale industry and has been uploaded on the BARC website [216].

Double tungstate: Single crystals of $\text{NaR}(\text{WO}_4)_2$ R: Bi and Gd having high density and radiation hardness are the promising materials that can be used as radiation detector for both

luminosity and calorimetric measurements (CERN like conditions). The role of oxygen vacancies/interstitial in the luminescence properties of tungstate has been discussed. The present study was aimed at analyzing the intrinsic luminescence characteristics and understand the role of oxygen (during crystal growth as well as annealing in various ambient) in Sheelite type double tungstates. For that purpose, this study was performed on $\text{NaLn}(\text{WO}_4)_2$ compounds with $\text{Ln} = \text{Gd}, \text{Bi}$.

(i) $\text{NaBi}(\text{WO}_4)_2$: Un-doped $\text{NaBi}(\text{WO}_4)_2$ (NBW) crystals were grown using the Czochralski technique in air ambient. Optical transmission, reflection and luminescence measurements were performed on optically polished single crystal disks. To study the effect of oxygen environment around W, one disc was annealed in air at 700°C for 6 h while the other disc was annealed at 700°C under high vacuum conditions (10^{-6} mbar) for about 1 h.

As-grown crystal shows an excitation band peak at 322 nm with a shoulder at 280 nm for a broad emission band peaking at 495 nm. In the case of annealed crystal two emission bands peaking at 460 and 510 nm could be well separated for photo excitation at different energies. The excitation band at 280 nm was found to be suppressed significantly in the case of crystal annealed in air. Excitation peak at a higher wavelength (322 nm) can be ascribed to excitons and is independent of annealing while the lower wavelength (higher energy) excitation at 280 nm could be inter-band transitions between O p and W d states. The annealing changes the energy structure of regular WO_4 complex due to defects in anion sublattices including interstitial oxygen and oxygen vacancies which subsequently influence the higher energy excitation as observed in the excitation spectra measured for the annealed samples. The temperature dependence of emission has been studied. In the as-grown crystals the PL intensity becomes half at ~ 145 K and completely quenched after 200 K. The activation energy for

thermal quenching for 495 nm emission was calculated to be about ~ 160 meV in the case of NBW crystals which is smaller than that of PbWO_4 (~ 200 meV). The observed temperature dependence of PL is also found to be consistent with the reported results for other AWO_4 - type crystals. Thermal quenching profile was also found different for vacuum annealed samples and even at room temperature, the PL could be observed for these samples. Present studies suggest a different thermal quenching of PL due to different growth conditions compared to those reported earlier in the literature for this class of materials. Consequently, the crystals having desired properties can be grown in a controlled ambient that could affect its luminescence characteristics in a desired manner.

The role of the excitons and localization of charge carriers was understood by comparing the spectral dependence of excitation, photoconductivity (PC), transmission, reflectivity and band structure calculation of the as-grown NBW crystal. The dependence of measured reflectivity matches well with that inferred from electronic band structure calculation. Only intrinsic photoconductivity could be observed in these crystals. The photoconductivity observed in the excitation region indicates that excitation leads to free charge carriers. These processes correspond to delocalized transitions unlike localized transitions in the case of PWO. Therefore involvement of mobile charge carriers in the luminescence and excitation processes may be one of the reasons for lesser activation energy of thermal quenching of photoluminescence observed in the NBW crystals as compared to that of PWO crystals. The effect of annealing on PC shows a lower threshold value due to the dissociation of excitons at defects created in the anion sublattice. The appearance of PC below absorption edge may be corresponding to the absorption band of O^- centers. Lower thermal quenching due to the presence of mobile charge carriers and intrinsic photoconductivity only in the excitation region make the NBW crystal a more

promising Cherenkov radiator compared to the PWO crystals that are deployed currently in the high energy physics experiments at the CERN.

(ii) NaGd(WO₄)₂: Un-doped and Yb³⁺ doped NaGd(WO₄)₂ [NGW] single crystals were grown by the Cz technique using an automatic diameter control system (Cyberstar oxypuller) under varying conditions. Phase formation was checked by X-ray powder diffraction pattern and crystals orientation were verified by recording Laue pattern employing Huber make Laue back-reflection camera. The UV-VIS-NIR spectroscopy of the crystal revealed that the UV band edge of the crystal grown in argon ambient shifted towards lower wavelengths compare to crystals grown in air ambient. This may be due to oxygen related defects. Furthermore, the crystals grown in air showed a broad absorption band throughout the crystal bulk and resulted in poor quality of the grown crystals.

The intrinsic luminescence spectra show an excitation peak centered at 260 nm and a broad emission peak at 485 nm. The intrinsic emission from the single crystals grown in air and Ar were compared and it was found that the oxygen related defects played an important role in fluorescence properties of the material. The crystal grown in Ar ambient showed best luminescence properties at room temperature. It was also found that Gd energy levels participated in the luminescence process that made the luminescence behavior of the NGW different than the other double tungstate.

Finally, as the NGW is a multifunctional material, the polarized NIR absorption spectra of the Yb doped NGW crystal (a laser material) was recorded in 850-1100 nm range. The emission spectra for excitation in 980-990 nm range was found in accordance with the reported values. Though it showed a peak at nearly 1011 nm it is composed of several peaks centered at

935, 965, 975, 994, 1010, 1022 nm. The total broadening of the emission peak is around 60 nm that may make it suitable for the tunable femto-second laser source. Thus it was established that by controlling the oxygen content in the growth ambient the optical and luminescence properties of the NGW could be tailored.

Mn doped CaF₂: CaF₂:Mn also known as TL-400, is an important material for the TL dosimetry. It has a single TL peak around 260°C and is linear for a wide range of doses, from 0.5 mGy to few kGy. The maximum glow-curve intensity is achieved for a doping of 2.5 at.%Mn. It is desirable to use transparent CaF₂:Mn samples to obtain better sensitivity, higher light output and repeatability for dosimetric applications. The difficulty in growing doped single crystals of this material arises from the high vapor pressure of MnF₂ that prohibited its incorporation in the CaF₂ crystal lattice during the growth under vacuum conditions. The difficulty in the growth of single crystals has been circumvented by using optically transparent ceramics (OTC) of this compound in place of single crystal. The OTCs have several advantages over the single crystal like homogeneity, ruggedness, low cost, relatively simple manufacturing process etc.

In this thesis the synthesis of CaF₂ transparent ceramics doped with Mn (2.5 at.%) has been described. These ceramics were found to exhibit properties comparable to the CaF₂ single crystal. CaF₂:Mn (2.5 atm.%) transparent ceramics were prepared by hot pressing of nano-powders. The nano-powder was synthesized by a co-precipitation method. The nano powder and prepared OTC were characterized for the phase identification using a X-ray diffractometer. The microstructure of nano powder and fractured OTC was studied using the SEM and SANS. The transmission in the UV–Vis range (200–1100 nm range) was recorded using a

spectrophotometer and in the IR region by FTIR spectroscopy while the photo-luminescence was recorded using a fluorescence spectrometer in the range 200–800 nm. Further the oxidation states of the Mn dopant in the OTC were determined using an X-ray photo-electron spectrometer (XPS) and the concentration was determined using a secondary ion mass spectrometer (SIMS). The dosimetric properties were investigated by irradiating the samples with a ^{60}Co gamma source.

The average grain size, after hot pressing of the nano-powder at 1000°C for 2 h, has been found to be around $100\ \mu\text{m}$ and the hot-pressed pellets showed no voids or porosity. The relative density of the OTC was greater than 99%, as measured using the Archimedes's method. The in-line transmission spectrum recorded for this ceramic in the UV-Vis region exhibited about 50% transmission at 800 nm that decreased at lower wavelengths with a cutoff around 200 nm. The quantitative analysis confirmed the presence of Mn doping in the OTC. Concentration of Mn was found to be in the range of 1-1.5 at.%. It appears that the total amount of Mn added to the solution did not incorporate into the lattice of CaF_2 OTC and evaporates during the high temperature processing.

The excitation and emission spectra of the Mn doped CaF_2 OTC showed the presence of excitation levels corresponding to ${}^6\text{A}_{1g}({}^6\text{S}) - {}^4\text{T}_{2g}({}^4\text{G})$ transitions of Mn^{2+} that was in agreement with the reported values in literature. In TL studies a single glow-curve at $\sim 260^\circ\text{C}$ was obtained. The minimum dose that could be measured was about 3 mGy. The wavelength of the emission spectrum recorded during photoluminescence and thermoluminescence was found to be the same (470 nm). This indicated the observed excitation bands in both the cases were due to internal transitions of Mn^{2+} . The dose linearity of the OTC was measured by irradiating the

OTC to different doses and measuring the area under the glow-peak. The sample was found to be linear up to the highest dose of 100 mGy used in the present work.

In conclusion an alternative of CaF₂:Mn single crystal in the form of optically transparent ceramic has been developed employing hot pressing of nano-crystalline CaF₂:Mn synthesized using a wet chemical processing method. The problem of inhomogeneous distribution of the dopant (Mn) in CaF₂ matrix was solved and it was shown that the CaF₂:Mn (OTC) would be a better material than the conventionally used opaque pellets in TL dosimetry applications. A doping concentration of 1.5 at.% Mn has been successfully achieved in the CaF₂ OTC in spite of sintering at high temperatures under vacuum conditions, as confirmed by XPS and PL measurements. The OTC having Mn²⁺ in the CaF₂ matrix exhibited promising characteristics to be used as a TL dosimeter for applications in the personal and environmental safety.

In this thesis three different kinds of approaches covering a broad field of material synthesis and single crystal growth employing different techniques were investigated. The effect of growth process on crystal growth and scintillation properties of Tl doped CsI has been established. Crystals were grown employing two methods, namely gradient freeze technique and the modified Bridgman technique. The grown crystals were subjected to different heat treatments to improve their scintillation properties. The technology to grow high quality, large size (55 mm diameter x 75 mm Length) alkali halide crystals, developed during the course of this work is available for transfer to industry. In oxide materials sodium double tungstate crystals were taken for the study. The single crystals were grown by the Czochralski technique under varying ambient conditions. The post-growth heat treatment under various ambient was successfully used to tailor the fluorescence and optical properties of the grown crystals. It was

found that oxygen has a high mobility at elevated temperatures in the double tungstates that makes them sensitive to ambient conditions during the growth. A process to fabricate OTC of $\text{CaF}_2:\text{Mn}$ was developed during the course of this work. It was demonstrated that the synthesis of $\text{CaF}_2:\text{Mn}$ OTC at lower temperatures and under a reducing ambient facilitates the incorporation of Mn in relatively higher amounts and minimizes the oxygen contamination, thus improving the TL-properties significantly.

Future scope:

- The crystal growth system developed will be upgraded to grow alkali halide crystals up to 75 mm diameter and 80-85 mm length and to grow new scintillator materials like $\text{LaBr}_3:\text{Ce}$, $\text{SrI}_2:\text{Eu}$, etc.
- Further studies will be carried out to probe and direct observation of the defects related to oxygen for better understanding of these defects employing various experimental techniques viz. Positron annihilation, EXAFS, ESR, ENDOR, etc. The effect of oxygen defects on lasing characteristic of Yb doped NGW will be studied.
- Further studies will be performed on the optimization of doping concentration of Mn in CaF_2 along with other co-dopants to improve the sensitivity and dynamic response range of the material.