SYNOPSIS

Single crystals have since long created a nice niche among advancement of technology that spans from the electronics and related development to generation of high power tuneable solid state laser and the radiation detection [1-6]. There have been continuous efforts in developing single crystals of new materials with better quality compared to existing one, to improve the quality of single crystals of the existing materials, making their growth easy by improving the growth conditions, or modifying the existing growth techniques for a better yield. In some cases where it is difficult or impossible to grow single crystals with desired properties like homogeneity in dopant concentration, researchers are trying to find a replacement of single crystals in the form of optically transparent ceramics (OTC) that show, in some cases, better properties than the single crystals for specific applications.

The research work of my thesis entitled "Effect of Growth Processes on Characteristics of Some Technologically Important Oxide and Halide Crystals" dwells on the growth of single crystals of a few materials that find applications as scintillator detectors and radiation dosimeters. The effect of growth parameters on their characteristics has been investigated mainly to improve their properties for the intended applications.

A large number of different scintillation crystals exist that are used for the detection and spectroscopy of wide assortment of radiations. A good scintillator should posses certain properties like high density and high Z-effective (stopping power for ionizing radiation), large range of linearity in response (Photon/MeV), transparency to its own emission, faster decay (high rate of pulse counting), suitable emission wavelength to match the photo-detector read out, etc. [7]. Similarly, the requisite properties for a good thermal dosimeter material (another kind of radiation detector) are: single glow curve (single type of trap centres) in the temperature range of 150-250°C, high sensitivity, repeatability, good light output, homogeneity in the trap centre distribution, easy preparation, inert to ambient, etc. However, no material simultaneously meets all these criteria, and the choice of a particular scintillator/dosimeter is therefore always a compromise among these and other factors for a given application. Most of the present scintillators and phosphors for dosimeters can be broadly classified in two categories consisting of halides and oxides compounds. The growth parameters and preparation procedures greatly affect, in terms of defect formation and dopant distribution, the scintillation process and other properties of the materials like radiation hardness, optical properties etc., in a favourable or adverse manner depending on the nature of defects and luminescence centre.

In the present research work I intended to study the effect of preparation procedure and growth parameters on the properties of a few oxide and halide materials including CsI:Tl and $NaBi(WO_4)_2$ and $NaGd(WO_4)_2$ based scintillator and Mn doped CaF_2 as a material for the thermally stimulated luminescent dosimeter. The aim of the study is 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.

In the following sections, the research work carried out on these materials and plan of presentation of results in the thesis have been briefly outlined.

Chapter- 1: Introduction

The first chapter of the thesis deals with a brief introduction to single crystals and their applications in various fields with an emphasis on their use as scintillators and phosphor materials in radiation detection and measurement. The scintillation process has been described in a general form and few important steps involved in the process along with some theoretical aspect have been described. The properties of an ideal scintillator are listed with their importance to the intended application has been explained. A brief history of inorganic scintillators along with their properties and preparation methods has also been given. A brief introduction to materials that are studied in the present work i.e. CsI, $NaBi(WO_4)_2$, $NaGd(WO_4)_2$ and CaF_2 along with their brief history is given.

Chapter-2: Experimental techniques

Among the three types of materials considered in the thesis, CsI, $NaBi(WO_4)_2$ and $NaGd(WO_4)_2$ are prepared in the form of single crystals. The crystals of CsI have been grown by a modified Bridgman technique while NRW single crystals have been grown using the Czochralski technique. The third material, Mn doped CaF_2, is developed in the form of optically transparent ceramic (OTC).

In this Chapter, techniques to grow single crystals have been described in general and Bridgman and Czochralski techniques in particular. Other experimental techniques like X-ray diffraction, Laue back reflection, spectroscopy, gamma-ray spectroscopy, etc employed to characterize the starting materials and grown crystals during the present research are described. In addition, results of theoretical electronic band structure calculations for CsI, CaF_2, $NaBi(WO_4)_2$ and $NaGd(WO_4)_2$ are also briefly given in Chapter-2.

Chapter-3: Growth of single crystal of Tl doped CsI by a modified Bridgman crystal growth technique

In this chapter two different approaches that yielded, with considerable ease, good quality device grade single crystals of Tl doped CsI have been described.

I. Growth of CsI:Tl crystals in carbon coated silica crucibles:

In this part, the growth of single crystal of Tl doped CsI in carbon coated fused silica crucibles by a gradient freeze technique has been described. 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 discussed. By analysing the 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, optimum conditions for the growth of crystals have been determined. The grown crystals exhibited good radiation hardness and excellent scintillation properties. Gamma-ray detectors were fabricated and characterized to study the effect of growth conditions on the scintillation properties of grown crystals.

II. Growth of CsI:Tl crystals using a modified Bridgman method:

In a different approach a modified Bridgman technique has been designed and developed to grow the CsI single crystal of 50 mm diameter and 60 mm length, in a simple and effective manner. In this part of Chapter-3, design and construction of the modified Bridgeman system employed for the crystal growth of Tl doped CsI are elaborated. A specially designed crucible along with the modified furnace was used to grow single crystal of CsI:Tl of 50 mm diameter and 60 mm length. By employing this technique the thermal and mechanical shocks to the crystal were minimized that reduced the day light coloration and enhanced the radiation hardness of grown crystals.

Scintillation properties of the CsI:Tl have been described in this chapter. Gamma-ray detectors employing CsI:Tl and P-I-N photodiode combination were fabricated and characterized. These detectors showed excellent resolution (<8%) at 662 keV suitable for use in the γ-ray spectroscopy application to identify radio-active nuclides.

Chapter-4: Growth of single crystal of $NaBi(WO_4)_2$ and $NaGd(WO_4)_2$ and study of the effect of oxygen stoiciometry on their scintillation properties

Single crystals of $NaBi(WO_4)_2$ and $NaGd(WO_4)_2$ having high density and radiation hardness are the promising new materials that may find applications as radiation detectors for both luminosity and calorimetric measurements. These materials are intrinsic scintillators wherein WO_4^{2-} group is responsible for the luminescence [8,9]. In this chapter the growth of single crystals of $NaBi(WO_4)_2$ and $NaGd(WO_4)_2$ has been discussed along with the effect of oxygen environment around W on the scintillation and optical properties of these crystals.

(i) $NaBi(WO_4)_2$:

In this section of Chapter-4, the growth of un-doped $NaBi(WO_4)_2$ (NBW) crystals using the Czochralski technique has been described and its luminescence and optical properties as a function of oxygen defects have been analysed. Optical transmission and reflection spectra of as-grown, oxygen annealed and vacuum annealed samples were recorded over the wavelength range from 200 nm to 800 nm. Photo-luminescence (PL) studies were performed over a wavelength range from 300 nm to 800 nm and in a temperature range of 77–300 K. The spectral dependence of photoconductivity was measured at an applied field of 500 V/cm on the same samples.

Photo-luminescence spectra of as-grown crystals consist of emission band at 495 nm and two excitation bands at 322 nm with a shoulder at 280 nm. A large stoke shift of 10,854 cm^{-1} for the emission band was found to be similar to other molybdate and tungstate crystals [10]. The effect of annealing on the luminescence process has been studied and discussed. The annealing induced changes in the energy structure of regular WO_4 complex has been analyzed using the reflectivity and PL spectra and photoconductivity measurements carried out on the as-grown and annealed samples. The temperature dependence of emission was also studied. The thermal activation energy for the quenching was calculated from a Mott–Seitz dependence of photoluminescence and found to be consistent with the PL quenching. Thermal quenching profile was also found to be changed for samples annealed in different ambient.

The electronic band structure of NBW was calculated and analysed. The presence of Bi states in valance band (VB) and conduction band (CB) suggest that the excitons may be created at Bi ions and then trapped at the $(WO_4)^{2-}$ complex. The role of these excitons and localization of charge carriers were understood by comparing the spectral dependence of excitation, photoconductivity (PC), transmission and reflectivity of the as-grown NBW crystal.

(ii) $NaGd(WO_4)_2$:

In this part of Chapter-4 the growth of un-doped and Yb^{3+} doped $NaGd(WO_4)_2$ [NGW] single crystals by the Czochralski technique under various ambient (pure Ar and air) has been described and the optical properties of the grown crystal as a function of growth ambient were studied.

The crystals grown in air ambient were slightly greenish in appearance due to oxygen related defects. The crystal grown in pure Ar ambient was black in colour, though it was crack-free and diameter was well controlled. This crystal (grown in Ar) when annealed at 800°C in air for 10 h turned transparent without any trace of blackness indicating a very high diffusivity of oxygen in the crystal. All the reflection in the powder X-ray diffraction of the grown crystal were in accordance to the crystal symmetry; space group I41/a (though few authors have reported I-4 non Centro-symmetric structure [11]). The Laue pattern was used to confirm the c-orientation of the crystal and its quality. The UV-VIS-NIR spectroscopy of the crystal revealed that the UV band edge of the crystal grown in argon ambient and annealed in air shifted towards lower wavelengths compared to crystals grown in air ambient. Further, the crystals grown in air show a broad absorption band which affects the crystal quality badly.

The intrinsic emission from the single crystals grown in air and Ar were compared. It was found that the intrinsic emission of the crystal grown in Ar ambient and annealed in air has different temperature dependence than that for the crystal grown in air and annealed. These findings suggest that the oxygen related defects play a significant role in optical and fluorescence properties of the material. Thus it was established that by controlling the oxygen content in the growth ambient one can tune the optical and luminescence properties of NGW crystals.

Chapter-5: Optically transparent ceramic of Mn doped CaF_2; a better material to substitute CaF_2:Mn single crystal for applications as radiation dosimeters

The CaF_2:Mn is an important phosphor material for use as the thermo-luminescence (TL) dosimeter. The difficulty in growing doped single crystals of this material arises from high vapour pressure and different crystal structure of MnF_2 that prohibit its incorporation in the CaF_2 crystal lattice during the growth under vacuum conditions and leads to variations in the Mn concentration throughout the crystal. The difficulty in doping single crystals with Mn can be surmounted by preparing optically transparent ceramics (OTC) of this compound. In this Chapter the synthesis and characterization of CaF_2 transparent ceramics doped with Mn (2.5 at.%) are reported.

The OTC of CaF_2:Mn was prepared by hot pressing of nano-powders. The nano-powders were synthesized by a co-precipitation method. The nano powder and prepared OTC were characterized for the phase identification using an X-ray diffractometer. The microstructure of nano-powder and fractured OTC was studied using the SEM. The transmission in the UV–Vis range (200–1100 nm range) was recorded using a spectrophotometer. The photo-luminescence was recorded using a fluorescence spectrometer in the range from 200 nm to 800 nm. Further the valance states of Mn 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. Thermally stimulated luminescence (TSL) glow curves were recorded for different doses using an indigenously developed thermo-luminescent dosimetry set-up.

The excitation and emission spectra of the Mn doped CaF_2 OTC show the presence of excitation levels corresponding to $^6A_1g(6S)$ – $^4T_2g(4G)$ transitions of Mn^{2+} [14]. The glow-curve from the OTC (10 mg) recorded after a gamma dose of 100 mGy shows a single glow-peak at 260°C. The minimum dose that could be measured was about 3 mGy. The wavelength of the emission spectrum recorded during photoluminescence and TSL was found to be the same (495 nm). This indicates the observed excitation bands in both the cases are due to internal transitions of Mn^{2+}. This fact indicates a possible formation of hole-traps. 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 is found to be linear up to the highest dose of over 100 mGy used in the present work.

Chapter-6: Summary and Conclusions

The findings of the research work have been summarized in Chapter-6 of the thesis. Three types of materials were taken for the study; two in the form of single crystal and third in the form of OTC. It has been shown that the growth procedure significantly affects the properties of crystals mainly due to the formation of various types of defects during the material preparation and crystal growth.

A modified Bridgman technique has been developed for the growth of the CsI:Tl crystal and the optimum growth parameters for the best scintillation properties were determined. The effect of oxygen stoichiometry on the luminescence and optical properties of double tungstates were studied and it was established that the luminescence properties of the material can be tailored by appropriately choosing the oxygen environment during the growth or post-growth thermal treatment of crystals.

An alternative of CaF_2:Mn single crystal in the form of optically transparent ceramic has been developed employing hot pressing of nano-crystalline CaF_2:Mn synthesized using a wet chemical processing method. The problem of inhomogeneous distribution of the dopant (Mn) in CaF_2 matrix was solved and it was shown that the CaF_2:Mn (OTC) would be a better material than the conventionally used opaque pellets in TL dosimetry applications.

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