CHAPTER 1

INTRODUCTION

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 the present 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 the effect of preparation procedure and growth parameters on the properties of a few oxide and halide materials has been investigated. These materials include CsI:Tl and $NaBi(WO_4)_2$ and $NaGd(WO_4)_2$ based scintillator crystals 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.

The first chapter 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 investigated in the present work, namely, CsI, $NaBi(WO_4)_2$, $NaGd(WO_4)_2$ and CaF_2 along with their brief history is given. The motivation behind the work of the thesis has also been described in this chapter.

## 1.1 Material science and technology

Materials science and technology are closely related to each other. Materials technology is a comprehensive discipline that begins with the production of goods from raw materials to processing of materials into the shapes and forms needed for specific applications. Materials technology is a constantly evolving discipline, and new materials and processes with additional benefits over their predecessors lead to new applications. For example, the technology of poly-crystalline silicon ingots has clear advantage over mono-crystalline silicon in terms of cost with small loss of efficiency. Materials Science is a multidisciplinary field that connects material properties to the material's chemical composition, micro-structure and crystal structure and is closely related to materials technology.

In modern age technologically important materials are used in the different forms like single crystals, nano-materials, alloys, glass etc. Among these forms of materials, single crystals or like materials are must in several applications like semiconductor industries, nuclear radiation detection, medical imaging, solid state lasers etc. Though the materials studied in this thesis are mostly used or can be used in nuclear industry, most of them are multifunctional and can be used in various other applications like solid state lasers, beam splitter, optical window etc. In this thesis, these materials are taken, for study, in two forms (I) Single crystals and (II) Optically

transparent ceramic (OTC); keeping in mind their application and thus choosing the most suitable form.

1.2 Single crystals and their applications

Materials having atomic arrays that are periodic in three dimensions, with repeated distances are called crystalline materials. A single crystal or mono-crystalline solid is a material in which the crystal lattice of the entire sample is continuous, unbroken with no grain boundaries. The difference in mono-crystalline, polycrystalline and amorphous material is shown schematically in Fig. 1.1.
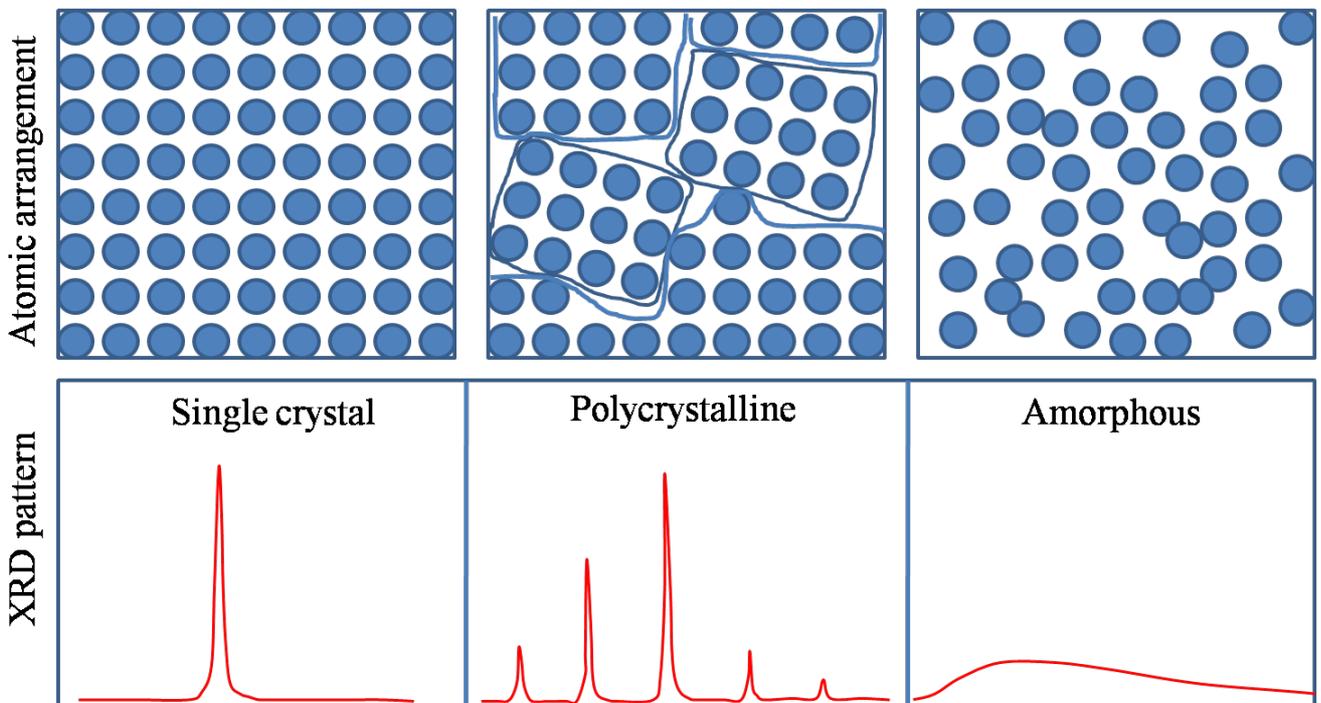

Figure 1.1: Cartoon showing the difference between single crystal, polycrystalline and amorphous forms of the material along with their XRD signatures.

Single crystals are the pillars of modern technology. Many of modern industries like electronic industry, photonic industry, radiation detection/imaging industry etc. depend on single crystals. Though it is more difficult to prepare single crystal than poly-crystalline material, the extra

effort is justified because of the outstanding advantages of single crystals. The reason for growing single crystals and its application in many fields is that many physical properties of solids can become obscured or complicated by the effect of grain boundaries like transparency, electrical conductivity etc. The main advantages of the single crystal form of a material are the anisotropy, uniformity of composition and the absence of grain boundaries. The strong influence of single crystals in the present day technology is evident from the continued advancements in the single crystal growth technology [3]. Hence, in order to achieve high quality single crystals at reasonable cost new crystal growth techniques are being developed or the old techniques are refined or modified.

As such applications of single crystals are very vast, but only a few fields are being mentioned here with the emphasis on scintillator and phosphor applications. A relative consumption of single crystals in various applications is given in Fig. 1.2. The field of semiconductor applications is omitted here as in this thesis only the optical crystals are considered.
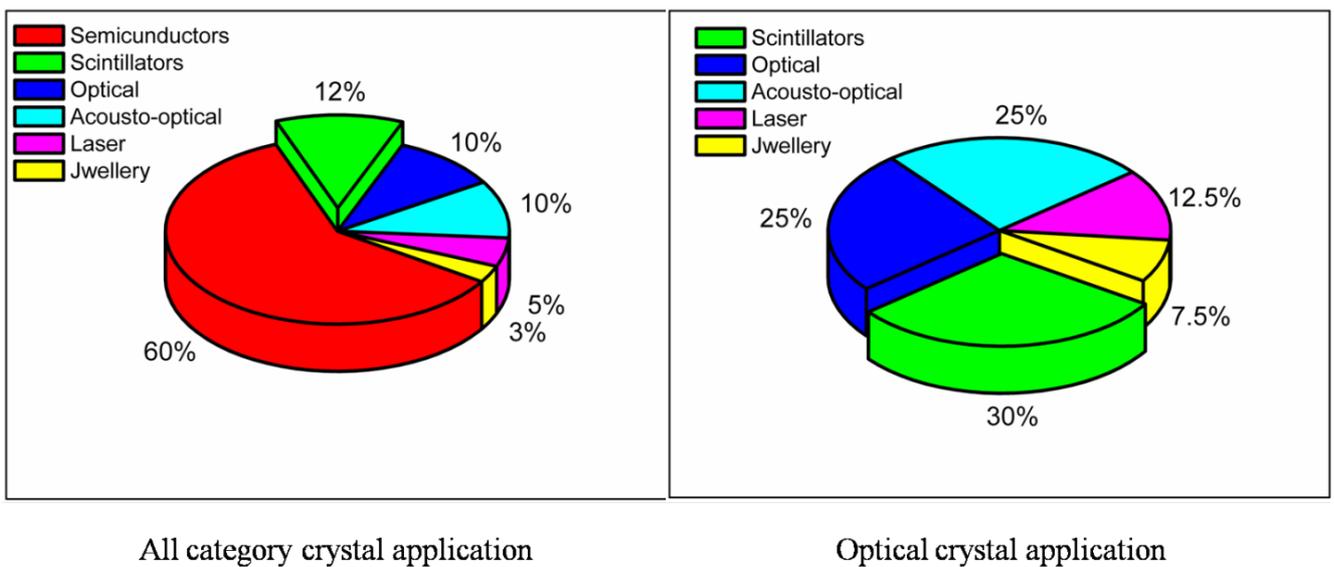
Figure 1.2: Pie-chart depicting applications of single crystals.
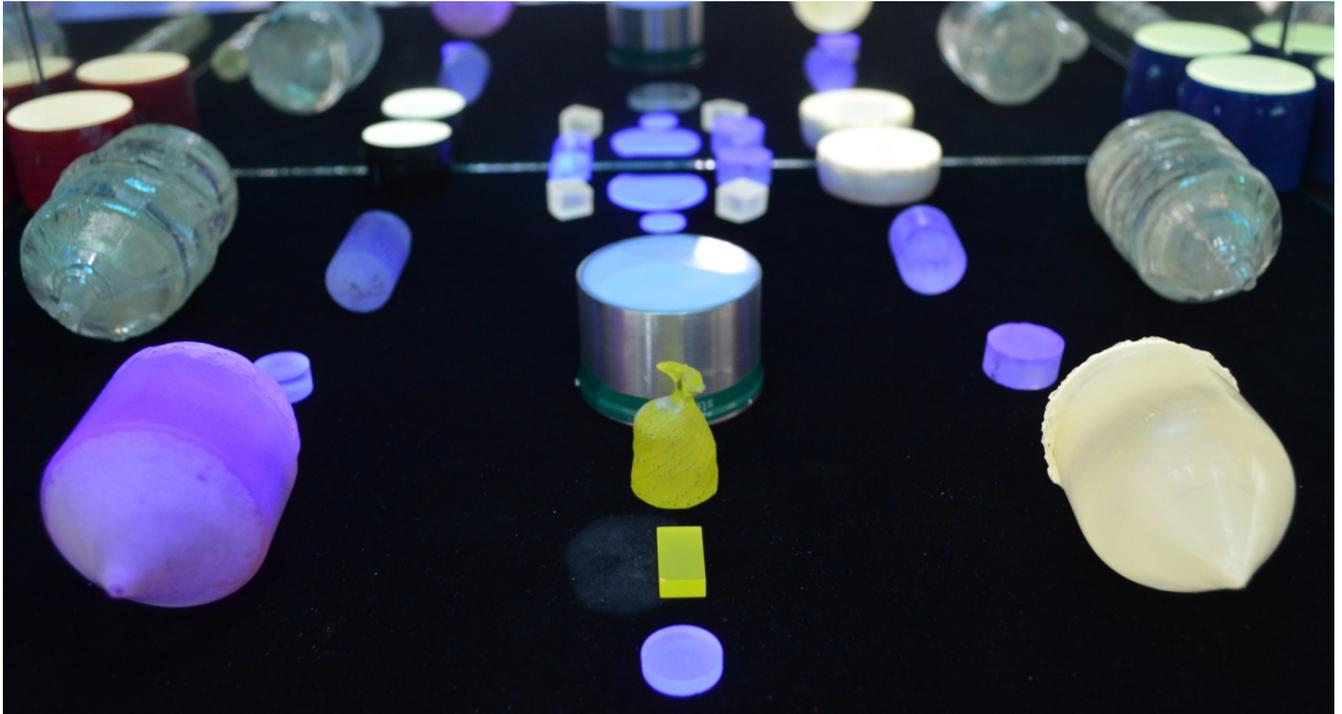
Figure 1.3: Photograph of scintillator crystals under UV illumination.

1.2.1 Scintillator and phosphor

Scintillation is a kind of luminescence processes. Luminescence can be excited in many different ways; by UV-photons, ionizing radiation (X-, γ-, α-, β-rays, charged particles, etc.), electron beam, or electric fields. Photograph of a few scintillator crystals (grown in our laboratory) under UV excitation is shown in Fig. 1.3. The core of the scintillation process is the transformation of energy of ionizing radiation into a variety of optical photons. The delayed scintillation is known as phosphorescence and the materials are called phosphors. The detailed explanation of scintillation process will be given in Chapter-2 of the thesis. The use of a scintillator to detect high energy radiation is century old science. Earliest scintillator that was used for the first time following Roentgen's discovery of X-rays was $CaWO_4$ [8,9], uranyl salts were used by Becquerel in 1896 to discover radioactivity, ZnS was used by Crookes and by Rutherford to study alpha particle scattering. All these scintillators were used as polycrystalline powder sheets

to detect the radiation by visual inspection or using a photographic plate [6]. Though the technique led to a number of important discoveries but it does not provide any spectroscopic information about the radiation and was obviously tedious. The period of visual scintillation counting ended in 1944 with the development of photomultiplier tubes (PMT) by Curran and Baker [10, 11]. The PMTs could convert the weak light flashes into measurable electric pulses that could be counted and analyzed electronically in modern-day devices.

Though the PMT was discovered in 1944 its full potential in radiation detection could be utilized only after the discovery of scintillation in Tl doped NaI in 1948 by Robert Hofstadter and availability of NaI:Tl in single crystal form [12]. The NaI:Tl was patented as a first scintillation material in 1950, and John Harshaw from Harshaw Chemical Company (US), initiated interest in growing NaI:Tl crystals by the Stockbarger method. Since then the single crystal growth process has been developed to a state-of-art level. The NaI:Tl is still the most widely used scintillation material and has the highest light yield among the commonly used scintillators. The spectrum of its applications is quite large and ranges from nuclear physics and nuclear medicine to geophysics and environmental measurements. In a burst of exploration during the following decades, variety of new inorganic scintillator were discovered (CsI, CsI:Tl, CsI:Na, $CdWO_4$, CaF_2:Eu, BaF_2 etc) and the growth and production process of scintillator single crystal were refined and perfected. Lithium-containing compounds used to detect neutrons and the first glass scintillators were also developed in the 1950s.

The past two decades have witnessed a great flurry and progress in research and development of scintillator materials, prompted to a major degree by the need for scintillators for precision calorimeters in high-energy physics, high photo-yield scintillators for medical imaging, geophysical exploration, and numerous other scientific and industrial applications [9, 13]. Few

excellent materials discovered in past two decades are $LaBr_3$:Ce, LuI_3:Ce, SrI_2:Eu, Lu_2SiO_5:Ce, Gd_2SiO_5:Ce, $Li_6Gd(BO_3)_3$:Ce, $Li_6Yb(BO_3)_3$:Ce, $PbWO_4$ etc. The discovery of $PbWO_4$ by L.L. Nagornaya [14] from the Institute for Scintillation Materials of Ukraine led to a revolution in the collider physics and created a base for the new generation of detection systems in high energy physics, starting from a calorimeter for CMS (LHC, CERN) and finishing with the project PANDA (DSI). Cerium doped Lu_2SiO_5 first discovered by C.L. Melcher [15] that has fast timing characteristic combined with a high light yield revolutionized the positron emission tomography (PET) technology providing unmatched spatially resolved 3D images in medical diagnostics. The Ce activated crystals $LaBr_3$ and $LaCl_3$ with high light yield and excellent proportional response show unprecedented energy resolutions for scintillator detector that was, a few decades back, thought unsurpassable by scintillator detectors.

Though there has been tremendous development in inorganic scintillators, still there are very active researches going on to develop better, bigger and cheaper scintillator crystals. Concurrent with the materials development and use of many new characterization techniques based on synchrotron radiation and laser spectroscopy, have led to a greater understanding of the complexities inherent in exciton and defect formation during and after crystal growth, and the numerous other processes involved in scintillation. These physical processes are now generally well understood and are being used to improve the properties of scintillator material by improving their growth processes [16].

1.2.2 Cherenkov detector

Apart from scintillator, Cherenkov radiation is an electromagnetic radiation emitted as a consequence of passage of charged particle through an insulator at speeds greater than speed of

light in that medium [17]. The energy of emitted radiation is proportional to the refractive index of that medium and phase velocity of charged particles passing through it. It is a continuous radiation in UV/visible range without any characteristic spectral peaks. The intensity is very high which is emitted nearly immediately unlike scintillation that occurs with a characteristic time constant. Generally, materials with high density, high refractive index, large band gap, and with no scintillation are better candidates for a Cherenkov detector [18]. Due to the absence of scintillation and high energy threshold for Cherenkov radiation these detectors are best suited for use in Beam end-caps as there is very high background of low-energy charged particles [19,20]. An energetic charged particle can be identified through the measurement of mass-dependent threshold energy of Cherenkov radiation if its momentum is known [21, 22]. Detectors based on Cherenkov radiation are used for particle physics experiments, nuclear reactors, astrophysics experiments, detection of bio-molecules, etc.

1.2.3 Laser host

The first solid state laser built in 1960 by T. Maiman was based on a pink ruby crystal (Al_2O_3:Cr). Since then the there has been tremendous development in the laser host materials and their growth techniques. Single crystals with very high optical quality and minimum defects are essential in the solid state laser applications. Solid-state host materials may be broadly grouped into crystalline solids and glasses. The host must have good optical, mechanical, and thermal properties to produce laser and withstand the severe operating conditions of practical lasers. Desirable properties include hardness, chemical inertness, absence of internal strain and refractive index variations, resistance to radiation-induced color centers, and ease of fabrication. Some of the most useful laser host materials are synthetic garnets: yttrium aluminum garnet,

$Y_3Al_5O_{12}$ (YAG); gadolinium gallium garnet, $Gd_3Ga_5O_{12}$ etc. These garnets have many properties that are desirable in a laser host material [23, 24]. They are stable, hard, optically isotropic, and have good thermal conductivities, which permit laser operation at high power levels. Vanadates (AVO_4: A-Y, Gd, Lu etc) and fluorides ($YLiF_4$:Nd) are other category of good laser host materials [25, 26].

Rare-earth doped double tungstate crystals $NaY(WO_4)_2$, $NaGd(WO_4)_2$, $NaLa(WO_4)_2$, $NaBi(WO_4)_2$, $KY(WO_4)_2$, $KGd(WO_4)_2$ etc. having a disordered structure are of current interest as high gain solid state host materials for lasers due to broad absorption lines of the dopants and low melting temperatures that make their growth easy compared to garnets and vanadates crystals [27, 28].

1.2.4 Others applications

Apart from above mentioned applications that are main theme of the thesis there are several other applications of single crystals.

Acousto-optic devices are based on the effect of propagation of sound waves on the refractive index of a medium, resulting in the formation of refractive index grating are called acousto-optic modulator (AOM). This acousto-optic interaction makes it possible to modulate the optical beam in both temporal and spatial domains by varying the amplitude, phase, frequency and polarization of the acoustic wave. These types of devices are extensively used in mobile communication devices. Single crystals of $LiNbO_3$, $PbMoO_4$, etc. are frequently used in many such applications [29, 30].

Optical window is a piece (mostly circular but sometimes rectangular, optically flat and parallel disc) of a transparent optical material that allows light (for a wavelength range of interest) into an optical instrument isolated from vacuum or other medium. Highly transparent optical windows from deep UV to far IR region are technologically important. The materials to be used in these applications should have large band gap, isotropic and of good mechanical properties. Most popular materials used in optical windows are CaF_2, LiF, BaF_2, ZnS, etc [31].

1.3 Optically transparent ceramics: an introduction

Optically transparent ceramics (OTC) are the highly compacted (to near theoretical density) polycrystalline bulk that show transparency in UV-VIS-NIR region. There are many applications that require optically transparent material like scintillator detector, solid state laser generation, optical window etc. Conventional optical transparent materials mainly include glasses, polymers and alkali hydrides, which have been widely used in industries and daily life. However, these materials have relatively poor mechanical strengths and sometimes insufficient chemical and physical stabilities. With the advancement in technologies in crystal growth, single crystals of some compounds appeared as new transparent materials. Compared to the conventional transparent materials, single crystals of many materials have desired properties and are being used in such application for the last five decades. However, growth of single crystals requires sophisticated facilities and it is time consuming, thus leading to expensive products that are only used in cases where cost is not the deciding factor. Machining of single crystals in various shapes to meet the requirement of specific applications is a difficult task and results in wastage of materials. The variation of dopant in the crystal bulk due to segregation coefficient other than unity is another difficulty faced in the single crystal growth. The non-

homogeneity in the dopant concentration may change several properties of a material like luminescence, refractive index, absorption etc. In some applications like thermal dosimetry where batch calibration is required, use of single crystals becomes very difficult. Other problems of single crystals include difficulty to produce in large quantities particularly for brittle materials. Even in case of few materials, that have tendency to decompose or phase change prior to melting, it is not possible to prepare single crystals. In this respect, transparent ceramics become more important. Transparent ceramics have various advantages over single crystals, such as cost-effectiveness, large-scale production, feasibility of shape control and better mechanical properties. Therefore in many applications optically transparent ceramics are proven superior to single crystals [32-33].

The most significant factor to the transparency of a ceramics is the porosity. The surface of a pore (generally filled with air or moisture) is a boundary between phases with sharply different optical characteristics, which therefore intensely reflects and refracts light. Therefore to make a polycrystalline material transparent it is necessary to remove nearly all the pores from the bulk. Pores could be intergrain or intragrain. The elimination of intragrain pores, even if they are submicron in size, is a more difficult and much longer process than the elimination of closed intergrain pores. Another reason of the opacity is the presence of secondary phases at the grain boundaries. Therefore, to fabricate transparent ceramics, it is necessary to use raw materials of high purity and to avoid any possible contamination during processing. Crystal structure and anisotropy in optical properties of a material pose some limitations over the OTC preparation. In ceramics of optically anisotropic crystals, an additional scattering of light arises at the boundaries when the light travels from one grain to another even if there are no pores in

between. This is the reason why transparent ceramics generally have a cubic lattice structure, which is isotropic, such as MgO, Y_2O_3, YAG, and $MgAl_2O_4$ (spinel) [34].

1.4 A literature survey

1.4.1 Alkali halides: Tl doped CsI, NaI

The era of inorganic scintillators materials begins with the discovery of NaI:Tl in 1948 by R. Hofstadter. Since then the alkali halides are at the forefront of this field despite discoveries of new and better scintillators. The chief advantages of these materials over the newly discovered $LaBr_3$:Ce and similar crystals are the cost effectiveness and large size production. Followed by the discovery of NaI:Tl, the thallium doped CsI was discovered by same person in 1950 [35]. The CsI:Tl single crystal is a well-known scintillator material, and has been deployed in a variety of applications owing to its moderate density, high light yield and suitably matched emission with photodiodes [36-39]. It shows better scintillation efficiency (if used with a suitable photo-detector), and is less hygroscopic and less brittle than NaI:Tl crystal. This material could not achieve its full potential in the past due to the unavailability of a matching photo-multiplier tube (PMT). However, the possibility to use compact silicon P–I–N photodiodes (PD) that show good efficiency at longer wavelengths and lower operating voltages has renewed the interest in the CsI:Tl crystals. The choice of the CsI:Tl-PD as a detector has been dictated by some considerations in terms of compact size, insensitivity to magnetic fields, reduction of cost and complexity, no requirement of high voltage power supply and mechanical robustness compared to the classical NaI:Tl scintillator with photomultiplier (PMT) read-out. Though, new materials like $LaBr_3$:Ce, $LaCl_3$:Ce etc. show superior scintillation properties, their peak emission in the 350 – 400 nm range makes them unsuitable for use with photo-diodes.

Further, most of these materials are also highly hygroscopic, brittle and expensive. Later Na doped CsI discovered by J. Menfee et al. [40] was proved an excellent scintillator similar to Tl doped NaI [41,42].

Single crystals of CsI can be grown using the Bridgman-stockberger method as well as the Czochralski method [43-46]. The growth of CsI crystals using the Bridgman method 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 [47]. These issues are important and need to be addressed to grow device grade crystals. In addition, the luminescence and scintillation properties, after glow, and radiation hardness etc of CsI:Tl are known to depend upon various stages of crystal preparation, viz.: starting material preparation, Tl concentration, growth technique and post growth annealing treatments [48-50]. Despite considerable efforts for many decades on this material, its poor radiation hardness and long afterglow are still major areas of concern that hinder its application to several other fields. It was found that despite being very old material, literature on the crystal growth of CsI and NaI employing Bridgman technique is less available and few problems like crystal recovery, after growth, annealing steps etc are not explained in details. The research in these fields may improve the crystal quality and make them more useful in radiation detection application.

1.4.2 Double tungstates: $NaBi(WO_4)_2$, $NaGd(WO_4)_2$

A large number of tungstate (AWO_4: where 'A' stands for large size divalent ions like Ca, Pb or Ba) are naturally occurring crystals. Their Scheelite structure is characterized by tetrahedrally coordinated $(WO_4)^{2-}$ group positioned at four corners of a unit cell and the divalent A^{2-} located at bcc is octahedrally coordinated with oxygen ions [51]. The research interest in tungstate

materials dates back to early 20th, with the use of $CaWO_4$ as scintillator [8]. In the late 20th century due to the demand from high energy physics crystals of $PbWO_4$ were developed and extensively used as scintillation detectors [52, 53]. Rare-earth doped double tungstates [Re:NaT(WO$_4$)$_2$ with T being a trivalent ion are also iso-structural to $PbWO_4$ having the same functional group $WO4^{2-}$. Therefore these materials have potential to be used in radiation detection application [54], though these are multifunctional material and are also of current interest in laser generation [55, 56].

Single crystals of NaT(WO$_4$)$_2$ T: 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) [57]. From the chemical point of view these materials may be regarded as related to $CaWO_4$ Scheelite-type compound with the replacement of Ca by a 1:1 mixture of R and Na. These materials are intrinsic scintillators and WO_4^{2-} group is responsible for the luminescence [58]. The W^{6+} is surrounded by four oxygen atoms in a regular tetrahedral environment. We consider a one-electron charge transfer process from the oxygen 2p orbital to the 4d and 5d of the W^{6+}. For the tungsten compounds, the ground state corresponds to the $^1A_1$ level (4d/5d^0 W6$^+$ /2p^6 O^{2-} state) and the lowest energy excited state results from the splitting of the $^3T_1$ level (4d/5d^1 W^{5+}/2p^{5}O$^-$ state) [59]. Therefore the absorption band is a charge transfer excitation band. After the relaxation processes through the different vibration levels of the excited state, electrons reach the more stable state of the lowest energy excited state (LEES) from which the system can emit photons. As the emission comes from a level associated to an electron transfer mechanism, it is described as charge transfer emission band. The energy difference between the maximum of the emission and excitation band related

to the same two levels is called Stokes Shift. This value gives information about the non-radiative contribution to the relaxation processes.

Tungstates in general are characterized by the presence of two emission bands in the blue and green regions that arise due to electronic transitions within WO_4 groups [60]. The relative intensities of these two emission bands depend on crystal stoichiomtery with regard to both cationic and anionic sub-lattices. Campos et al. [61] and others explained experimentally and theoretically the phenomena responsible for luminescence in $CaMO_4$ (M = W, Mo). The blue-green emission comes from the slightly distorted WO_4^{2+} tetrahedra, while the orange comes from a distortion in the long and medium range orders. Though there have been extensive studies on the effect of growth ambient and annealing on the luminescence and scintillation properties of $PbWO_4$ and other single tungstates [62-64], literature on the growth ambient effect on the luminescence properties of double tungstate is lacking. The present study aims to analyze the intrinsic characteristics of the structure and role of oxygen (during crystal growth as well as annealing in various ambient) in order to know about the role of oxygen in the intrinsic luminescence of the sodium double tungstates.

1.4.3 Fluoride: Doped and undoped CaF_2

The CaF_2 is among the earliest known thermo-luminescence (TL) emitting materials [65-67]. A variety of dosimeters based on Mn or rare earth elements doped CaF_2 have been developed over the years [68-70]. Mineral of CaF_2 is formed in nature in the form of crystalline blocks. Due to its large band gap (~8 eV) it shows a variety of hue and brilliant luminescence on the incorporation of impurity ions. Undoped CaF_2 single crystal is an important optical material with high transmission in a broad wavelength range (165 – 1600 nm) and used as IR windows

and other types of optical components such as lenses, prisms, etc. [71]. On the other hand, doped CaF_2 is a multi-functional material that finds applications in laser production (CaF_2:Yb) [72, 73], as radiation detectors (CaF_2:Eu) [74] and as a thermo-luminescence (TL) dosimeter (CaF_2:Dy, CaF_2:Mn, CaF_2:Tm) [75]. The CaF_2:Mn is also a known TL dosimeter called as TL-400 [76]. It has a single TL peak at around 260°C and is linear for a wide range of doses, from 0.5 mGy to few kGy. However, the TL curve depends on the Mn concentration [77] and the maximum glow curve intensity is achieved for a doping of about 2.5 at.% Mn. It is desirable to use transparent CaF_2: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 MnF_2 that prohibits its incorporation in the CaF_2 crystal lattice during the growth under vacuum conditions. It also leads to variations in the Mn concentration throughout the crystal. Hence, most of the reports on this material are either on polycrystalline powder samples or pellets [77, 78]. The difficulty in the growth of single crystals can be circumvented by using optically transparent ceramics (OTC) of this compound. Recently, fabrication of CaF_2 transparent ceramic doped with Yb, Eu, Er has been reported in literature. Except for CaF_2:Yb applications of these transparent ceramics have not been fully explored yet. In the present thesis the synthesis of CaF_2 transparent ceramics doped with Mn (2.5 at.%) is reported. These ceramics were found to exhibit TL properties superior compared to the CaF_2 single crystal.

1.5 Scope and Aim

The material properties like transmittance, luminescence, radiation hardness etc are highly dependent on the defect centers in the bulk. Various types of defects viz point defects, linear

defects (screw and line dislocation), grain boundaries, stacking faults etc. are inherently present in crystals [79]. Color centers, most numerously found defects are basically point defects arising due to lattice vacancies, interstitial atoms (self trapped and impurities) and substitutional impurity ions. They play deterministic role in the optical and emission/scintillation properties of the crystal. These defects act as trap centers resulting in the formation of optical absorption bands in transparent region. These defects may be formed due to elemental impurities or inherently during the material preparation due to growth ambient, stoichiometric variation, thermal and mechanical shock, etc.

The partial oxygen pressure during the material preparation or crystal growth is known to affect the scintillation mechanism to very large extent by creating either oxygen vacancies/interstitial and by changing the oxidation state of dopants. For examples single crystals of Ce doped Lu_2SiO_5 grown in various partial oxygen pressure show different light output due to changes in the Ce oxidation states and emission spectrum [80]. On the other hand, the scintillation decay times of Ce-doped $Gd_3Al_3Ga_2O_{12}$ depend on the oxygen content in the growth atmosphere; crystals grown under a high oxygen concentrations show faster decay time than the one grown under a lower oxygen concentration [81]. Similarly Ce doped $YAlO_3$ is also known to be very sensitive to the growth ambient [82]. In case of halides like NaI and CsI and fluorides, oxygen plays a major role in the defect formation during dehydration and growth processes by creating iodine/fluorine vacancies and F centers. These defects considerably decrease the radiation hardness and increase the afterglow thus adversely affecting the scintillation performance of the material. Oxygen content in the growth atmosphere thus appears to be an important parameter in the optimization of the growth process of scintillation materials that can be used to tailor the performance of the scintillators.

The stoichiometric variation during the growth of the multi-component materials due to selective evaporation or segregation of one of the constituent element or compound is another parameter that affects the crystal quality and properties. For example during the growth of $PbMoO_4$ single crystal the selective evaporation of MoO_3 creates various defects that in turn generate crystal cracking and coloration [83]. On the other hand during the growth of $PbWO_4$, the melt become progressively deficient in PbO that affect the crystal quality. To solve these problems the initial material is taken in an off-stoichiometris composition compensate for the excessive loss of one of the components, for example in the case $PbMoO_4$ and $PbWO_4$, MoO_4 and PbO respectively are taken 1-2% excess in the initial material. In some cases pre-crystallized charge is also used to solve this kind of problem.

The defects are also formed due to the thermal and mechanical stresses generated during the crystal growth. The thermal and mechanical shocks faced by a crystal highly depend on the crystal growth technique. Like in the Czochralski growth technique (RF heating) growing crystal faces large thermal shock as the free crystal surface is continuously in contact with ambient air flow and is subjected to very high temperature gradients. While in a Bridgman furnace the mechanical stresses exerted by crucible walls on the growing crystal during the growth and cooling are high. These shocks generate stresses in the crystal that are one of the reasons of crystal cracking.

The segregation of the dopant during the crystal growth is another issue faced by crystal growers. This creates non-uniformity in the dopant distribution in the crystal that in turn affects the optical and scintillation properties of the crystal. In case of scintillation the light-output response of the scintillator becames position dependent that degrades the resolution of the radiation detector fabricated using these crystals. Further, the refractive index variations play a

detrimental role in the laser crystals and make lasing action impossible if the variation is beyond a certain limit.

It is well established that defect density plays a deterministic role in device applicability of a crystal and its control is quite challenging. There are continued efforts to grow single crystals with least defects and maximum uniformity by improving the growth process and developing new growth techniques. The development of processes to grow crystals with tight specifications for light yield, decay time and radiation damage, pose challenging problems to be solved by experts working in different fields of material science. This requires a multidisciplinary approach, with a good coordination of efforts and a well-organized support. To solve the growth problem it is very important to understand the effect of growth process on the defects and the crystal quality. There are many advance techniques to probe the defects experimentally like optical absorption, thermoluminescence or electron spin resonance (ESR) techniques, scintillation characteristics etc. The effect of many defect centers (color centers) on electronic band structure can be simulated by first principles calculations that then can be identified experimentally and the true nature of the defect center may be found. A deeper understanding of color centers could be obtained through band formalism and calculations of electronic band structure and supported by detailed experimental work.

The scope of this thesis is to study the effect of growth processes on some technologically important crystals. Three kind of material ware considered for the study with the major emphasis on their scintillator and phosphor characteristic. The main aim is to develop suitable growth processes (mainly involving the growth techniques, the growth ambient and after growth thermal treatment) to grow crystals with desirable properties. In one case (Mn doped CaF_2) a better substitute for single crystal has been developed.