# Growth and Characterization of Li<sub>6</sub>R(BO<sub>3</sub>)<sub>3</sub>:R (R:Rare Earth ions): Promising neutron detector

By

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# **Homi Bhabha National Institute**

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## DECLARATION

L hereby declare that the investigation presented in the thesis has been carried out by me. The work is original and has not been submitted earlier as a whole or in part for a degree / fiploma at this or any other Institution / University.

> Awala kishin Sol Awadh Kishore Singh 10/05/2018

## List of Publications arising from the thesis

### Journal

- "A Comparative study of Li<sub>6</sub>R(BO<sub>3</sub>)<sub>3</sub>:Ce [R = Gd, Lu and Y] single crystals for thermal neutron detection", <u>A.K. Singh</u>, M. Tyagi, S.G. Singh, D.G. Desai, S. Sen, and S.C.Gadkari, *Phys. Status Solidi A* 2018, 1800224 (01-06).
- "Performance characteristics of thermal neutron detectors based on Li6Y(BO3)3:Ce single crystals", A. K. Singh, M. Tyagi, S. G. Singh, B. Tiwari, D. G. Desai, Shashwati Sen, S. S. Desai, S. S. Ghodke and S. C. Gadkari, *Nuclear Instruments and Methods in Physics Research* A 804 (2015) 189 193
- "Understanding energy transfer in Ce doped Li<sub>6</sub>Gd(BO<sub>3</sub>)<sub>3</sub>: A study of millisecond decay kinetics in 77–300K range", A.K. Singh, M.Tyagi, S.G.Singh, D.G.Desai, Shashwati Sen, S.C. Gadkari, *Journal of Luminescence*, 137 (2013), P-208–213.

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## **DEDICATIONS**

This thesis is dedicated to my family and friends

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#### <u>SYNOPSIS</u>

Radiation corresponds to the release of energy in the form of charged particles or electromagnetic radiation in a nuclear or electronic process. Any emitted particle/radiation during these fundamental processes will have sufficient energy to ionize the medium directly or indirectly through which they travel. Therefore, nuclear radiation is also known as "ionizing radiation", and detecting this ionization allows us to understand the nuclear processes involved. Radiation exist in nature due to the background from radioactive sources and other nuclear processes in the universe or artificially produced from man-made machines (reactors and accelerators) that are used for energy production, research, medical imaging, cancer treatment etc. Therefore, it is important to know the nature and the quantum of radiation to understand the physical process involved and reduce the health hazards that may arise due to the exposure of radiation to human.

The interaction of radiation with the medium is governed by the nature and energy (which can vary from a few meV to TeV based on its origin) of the ionizing radiation. They may interact with materials leading to the deposition of energy either partially or fully in the medium or may leave it without any interaction at all. A detector refers to an instrument that gives a measurable signal either in the form of an electronic pulse or a light pulse when it is exposed to radiation. It can be either active (Semiconductor detectors, Scintillators) which can instantly responds to the radiation or passive (dosimeters) where it can store history of the radiation exposure that can be read out later. Scintillation detectors generate photons when exposed to the charged particle radiation, electromagnetic radiation and neutrons. The photons generated in these detectors are proportional to the energy of the radiation and are coupled to light sensors to generate electronic signals which are easy to process, amplify and transport. Scintillation detectors can be used to detect charged particle radiation, electromagnetic radiation and neutrons and are preferred in some applications over other detector types due to fast read out, ruggedness and better efficiency. Among all radiations, neutrons are difficult to detect due to their limited interaction with the medium resulting in indirect or secondary ionization. Neutron detectors find several applications in research, defence, security and nuclear industries.

The conventional neutron detectors are based on <sup>3</sup>He and BF<sub>3</sub> gas filled chambers. While BF<sub>3</sub> is corrosive and toxic, the shortage of <sup>3</sup>He has made it prohibitively expensive. Due to the dwindling supply of <sup>3</sup>He, and the advent of spallation neutron sources, the need to explore alternative detector materials with a higher efficiency has arisen strongly. Among these new detectors, scintillators for thermal neutrons are currently explored extensively owing to their advantage over conventional detectors. Most of these scintillators for neutrons contain either lithium or boron or both due to their high cross-section for thermal neutrons. An ideal composition of a scintillator material should contain a large number of these atoms per unit cell to increases the chances of interaction of neutron with them. Lithium rare-earth borates are a common host material for scintillators which were earlier explored as laser hosts owing to their high band gap to allow the band gap engineering for tailoring the luminescent properties. This host lattice has been chosen for the research due to the presence of both boron and lithium and their large atomic density per unit cell. The large band gap allows incorporating rare-earth ions like cerium as an activator in the matrix to achieve a higher light along with fast decay characteristics from the activator.

In the present work, single crystals of lithium rare-earth borates doped with cerium were grown and characterised for their optical, electronic and scintillation properties. Single crystals of Li<sub>6</sub>R(BO<sub>3</sub>)<sub>3</sub>[R=Gd, Lu and Y] (LRBO) doped with cerium, have been proven as a promising scintillator for neutrons which contains <sup>6</sup>Li(natural abundance 7.4%,  $\sigma_{abs} = 940$  barns) and <sup>10</sup>B (natural abundance 20%,  $\sigma_{abs} = 3835$ barns) that produce charged particles after the interaction with thermal neutrons [1]. The charged particles generated in <sup>10</sup>B (n,  $\alpha$ ) <sup>7</sup>Li

and <sup>6</sup>Li (n,  $\alpha$ ) <sup>3</sup>H reactions excite the Ce<sup>3+</sup> ions resulting in a fast (30-50 ns) and efficient emission in the range of 400-450 nm. This matches well with the efficiency response of bialkali photomultiplier tubes (PMT) and therefore can be easily read out using the standard electronics. A lower effective atomic number (Z<sub>eff</sub>) of the LRBO also makes them less sensitive to gamma radiation for the mixed field detection.

Single crystals of cerium doped lithium gadolinium borate [Li<sub>6</sub>Gd(BO<sub>3</sub>)<sub>3</sub>: LGBO], lithium lutetium borate [Li<sub>6</sub>Lu(BO<sub>3</sub>)<sub>3</sub>:LLBO] and lithium yttrium borate [Li<sub>6</sub>Y(BO<sub>3</sub>)<sub>3</sub>:LYBO] were grown from melts using the Czochralski technique and extensively investigated by various characterization techniques. Optimized phase synthesis conditions have been achieved by employing several sintering schemes and performing phase analysis using powder X-ray diffraction (XRD). The thermal properties of the borates were studied by Thermo-gravimetric/Differential Thermal Analyzer (TG-DTA) to understand their melt behaviour to decide various parameters during the crystal growth to grow transparent and crack-free crystals. The luminescence properties of the grown crystals were studied using photoluminescence (PL) measurements to understand their electronic properties. The detectors were eventually fabricated from the as-grown crystals and were characterized for their scintillation performance under exposure to thermal neutrons.

The optical, electronic and scintillation properties of these three single crystals have been compared. In case of LGBO crystals, the decay characteristics were found to be affected with the energy transfer from gadolinium to cerium which makes the photoluminescence decay of the order of microseconds. Additionally, the presence of gadolinium, having very large thermal neutron capture cross section, resulted in the production of a continuum gamma showers which overrides the pulse-height spectra generated from thermal neutrons interaction with <sup>6</sup>Li and <sup>10</sup>B. Therefore, replacement of gadolinium with lutetium has been attempted to solve the poor discrimination and slow decay kinetics problems. However, this approach presented other problems in the single phase synthesis and poor crystal growth yield as compared to other borates in this family. Finally, the replacement of yttrium in place of gadolinium/lutetium resolved the slow decay kinetics along with better crystal growth yield among these three members of the borate family. A detectors setup based on this scintillator showed well define photo-peaks in the pulse-height spectrum generated from <sup>10</sup>B and <sup>6</sup>Li upon exposure to thermal neutron radiations. The detectors fabricated using cerium doped lithium yttrium borate doped crystals have been employed to detect thermal neutrons flux ranging from 10n/cm<sup>2</sup>/s to 10<sup>5</sup>n/cm<sup>2</sup>/s.

The research work carried in the present case out is compiled in the form of thesis and has been grouped under seven chapters as follows:

#### Chapter 1: Introduction

This chapter discusses methods of thermal neutron detection and various types of neutron detectors currently used in different applications. The basic mechanism to detect neutrons (a neutral particle) is based on indirect methods commonly consisting of the absorption of neutrons in a medium followed by the release of charged particles or photons often referred to as an (n,  $\alpha/\gamma$ ) reaction. However, a suitable interaction mechanism has to be chosen for the detector operation to detect neutrons in a particular energy range. Neutrons with energy less than 0.025 eV are classified as thermal neutrons while those in the range of 0.025 to 0.5 eV are classified as slow and those with energies greater than 1 keV are known as fast neutrons. Neutron detectors can be usually classified as the gas based detectors, scintillation detectors or semiconductor detectors. Gas based detectors filled with <sup>3</sup>He and BF<sub>3</sub>as the interaction medium is the most common thermal neutron detectors that have better gamma discrimination. These detectors are widely used for homeland security and defense, neutron basedfundamental research (e.g. neutron scattering beam lines etc.) and industrial monitoring

(e.g. personnel monitoring, water content in soil, etc.). <sup>6</sup>Li loaded glasses and liquid based scintillators are also used in certain applications employing the high Q value produced in the interaction with thermal neutrons. However, in the single crystal form the detector offers a higher efficiency due to higher atomic density, compact size and fast counting capability if doped with suitable activators (Ce<sup>3+</sup>). Single crystals based scintillators are radiation hard and show better mechanical strength for applications in harsh environmental conditions. Extensive literature survey was done to understand the characteristics of an ideal neutron detector and the areas of applications. Material selection for neutron detectors has been done on the basis of existing literature and the scope of research has been formulated on the basis of results and characteristics.

A brief introduction to cerium doped lithium rare-earth borates and the challenges to realize in the form of single crystals have been presented. The salient features of thermal neutron detectors based on scintillator crystals have been presented.

#### Chapter 2: Experimental techniques

This chapter presents various methods and techniques to grow single crystals from melts. The single crystals studied in this work have been grown by the Czochralski techniquewhich has been described in details. A description of various characterization techniques used in this work has been elaborated. Compositional and structural characterization techniques used for this work include powder X ray diffraction (XRD), Thermo-gravimetric/Differential Thermal Analyzer (TG-DTA) and Laue reflection patterns. For electronic characterization, UV-VIS spectrophotometer, photoluminescence spectrometer and X-ray stimulated luminescence techniques have been used in the present work and the mechanism has been described in this chapter. The Scintillation characterization and fabrication of thermal neutron detectors from as-grown single crystals have been described.

#### Chapter 3: Growth and characterization of Li<sub>6</sub>Gd(BO<sub>3</sub>)<sub>3</sub>

This chapter describes results on the growth of single crystals of cerium doped lithium gadolinium borate [Li<sub>6</sub>Gd(BO<sub>3</sub>)<sub>3</sub>:LGBO].Challenges in the synthesis of a single phase LGBO material and approach to optimise parameters to grow single crystals have been elaborated. A single phase LGBO material has been successfully synthesized using the solid state sintering method. The phase of the material has been verified by DTA and XRD techniques. The DTA pattern of the as-prepared material showed a large super cooling (~150°C) and a very narrow freezing profile (width <1.5°C), which was a major problem to grow single crystals from their melts. To overcome this problem a large axial temperature gradient of around 100°C/cm (just above the melt) was employed. Further, to avoid cracking of the grown LGBO crystal in a high temperature gradient due to the presence of cleavage planes, lower pull rates (< 1 mm/h) were employed in each growth run. Both, undoped and cerium doped single crystals of Li<sub>6</sub>Gd(BO<sub>3</sub>)<sub>3</sub> have been successfully grown from melts using the Czochralski technique. The grown crystals were characterized for their optical and electronic properties using transmission and photoluminescence measurements. Transmission spectra of undoped crystal showed sharp absorption lines below 350 nm corresponding to various transitions of Gd<sup>3+</sup> ions in the LGBO matrix. The wide absorption bands in the region of 350 nm were observed in the doped crystals due to the charge transfer bands from  $Ce^{4+}$  to  $O^{2-}$ . The emission spectrum of LGBO:Ce at room temperature consists of two bands centered at 313 nm and 400 nm. The band at 400 nm corresponds to the transitions in Ce<sup>3+</sup> centers in the LGBO matrix and the 313 nm band is attributed to the  $Gd^{3+}$  emission. The temperature dependence of the emission at 400 nm shows a decrease in the emission intensity when excited at  $Ce^{3+}$ centers due to the thermal quenching. However, the emission intensity stays nearly constant when excited at Gd<sup>3+</sup> centers mainly due to the charge transfer from Gd<sup>3+</sup> to Ce<sup>3+</sup> centers. The energy transfer process from  $Gd^{3+}$  centers to  $Ce^{3+}$  centers in the LGBO slows down the decay

characteristics of the emission in LGBO. This is not a desirable property for the scintillator and hence the gadolinium was planned to be replaced with lutetium.

#### Chapter 4: Growth and characterization of Li<sub>6</sub>Lu(BO<sub>3</sub>)<sub>3</sub>

In this chapter the single crystal growth and characterization of cerium doped  $Li_6Lu(BO_3)_3(LLBO)$  has been discussed. Single phase synthesis and crystal cracking were major challenges faced during the growth of LLBO single crystals. Although XRD pattern did not show any impurity phase, possibly due to a very low concentration of the foreign phases, the DTA pattern invariably showed the formation of some intermediate phases either during heating or cooling sequence. Several single crystal growth experiments were carried out and transparent crack-free crystals were obtained with optimized parameters. However, the crystal yield was very low as compared to that of LGBO growth. A similar broad emission peak near 400 nm has been observed corresponding to the 5d $\rightarrow$ 4f transition from Ce<sup>3+</sup>. The decay profile of the emission at 410 nm due to cerium centers showed a single exponential decay having decay time of ~ 30 ns. However, a low crystal growth yield mainly due to the presence of secondary phases formed during cooling, poor pulse-height and background from lutetium (Lu<sup>176</sup>) radioisotope were the major problems. These were addressed by replacing the lutetium with yttrium in the LRBO matrix.

## Chapter 5: Growth and characterization of Li<sub>6</sub>Y(BO<sub>3</sub>)<sub>3</sub>

This chapter deals with the growth and characterization of cerium doped  $Li_6Y(BO_3)_3$  (LYBO) single crystals. The optimized single crystal growth parameters are described and the optical and electronic characterization results have been presented in details. Single crystals of 0.1 % and 0.2 % cerium doped LYBO were grown in both argon and air ambient mainly to control the oxidation state of cerium. Transmission spectrum showed over 80 % transmission with

charge transfer band dominating in the region of 350 nm due to which the absorption bands of the  $Ce^{3+}$  centres could not be well resolved. However, photoluminescence measurements showed a broad emission band near 400 nm and the excitation bands at 300 nm and 350 nm arising from  $Ce^{3+}$  centres. Temperature dependent PL measurements showed thermal quenching in samples grown in argon ambient whereas the sample grown in air ambient showed no such features. Further, the decay profile fits into a double exponential decay with an average life time of about 25 ns which is a characteristic of the  $Ce^{3+}$  emission.

#### Chapter 6: Fabrication of neutron detector and measurements

This chapter describes the fabrication of solid state neutron detectors based on the single crystals scintillators. As-grown crystals were cut and polished in a cylindrical shape and detectors were fabricated in size of 10 x4 x 2 mm<sup>3</sup>. The polished crystals were wrapped with at least six to eight layers of reflective Teflon for an efficient collection of light by the photosensor. The fabricated scintillators were mounted on photomultiplier tubes and SiPM using optical grease. In case of a photomultiplier tube, the processing electronics consists of a preamplifier, a shaping Amplifier and a 1k MCA on an onboard commercial electronics (Gspeck) which also consists of a DC-DC converter to supply the high voltage to the PMT using power from a USB port of a computer. The pulse processing chain in case of a detector mounted on a silicon photo-multiplier (SiPM) consists of a shaping amplifier and an 8kTukan MCA. The detector has been used to detect charged particles, gamma radiation and neutrons in the pulse mode. The detector showed poor sensitivity to gamma-rays and a relatively larger Compton background has been observed at lower channels as a result of thin size and low Zeff of the detector medium. This was desirable as the detector was intended to be used in a mixed background of gamma and neutrons such as nuclear reactor buildings. The Pulse-height spectrum due to thermal neutrons consists of two peaks arising due to the <sup>6</sup>Li and <sup>10</sup>B interactions. The peak due to Li<sup>6</sup> reaction has been observed at nearly five times higher channel number due to higher Q value of the nuclear reaction and lesser quenching by the generated lighter charged particles. The peaks due to thermal neutrons in the PHS have been confirmed by covering the entire detector with a thick borated rubber or cadmium sheet, resulting in the disappearing of the photo-peak. Finally the detector has been calibrated at a standard neutron facility (flux of 250n/cm<sup>2</sup>/s and 150n/cm<sup>2</sup>/s)to calculate the efficiency of the detector.

#### Chapter 7: Conclusion and future scope of work

The LYBO based neutron detectors showed a better scintillation performance as compared to the detectors based on LGBO and LLBO single crystals. The LGBO turns out to be a slow detector with a poor neutron discrimination capability due to the presence of gadolinium that interacts with thermal neutrons and creates a continuum gamma shower. On the other hand, the detectors based on LLBO were fast to handle high counting rates but had lesser light-yield in comparison to the LYBO detectors. Due to this the peaks due to boron or lithium reaction are close to the background. Hence, neutron detectors have been fabricated based on LYBO scintillators and neutron measurements have been carried out in several neutron fluxes in the range from  $10n/cm^2/s$  to $10^5 n/cm^2/s$ . However, some aspects of the material engineering and further development of the detectors based on advanced photo-sensors keep the topic wide open for the future scope of work.

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## **CHAPTER-1**

## **Introduction**

#### **1.1 Background (Radiation detectors)**

Radiation is the emission of energy in the form of electromagnetic waves like gamma, X-rays etc., charged particles like alpha, electrons etc., and neutral particles like neutrons, antineutrino etc. It is usually emitted during fundamental physical processes causing direct or indirect ionization[1]. The advancement in the technologies for benefit of human kind has also increased the human interaction with radiation and therefore it has become important to know the nature and the quantum of radiation to use it constructively and reduce the health hazards due to undesirable exposure[2]. At the same time, it is also required to understand the fundamental physical process for further development of scientific content and development of technology for society. Most of the today's advance medical imaging techniques are an outcome of the work in this field over the last few decades[3,4].

To detect these radiations, we need a physical process which may convert the energy of these radiations in to some measurable form. A radiation detector works primarily on this principle and employs one or more physical processes to convert the energy of the radiation into either visible light (Scintillators) or charge (GM counters or semiconductor based detectors) that can be eventually processed into some electronic form. This electronic pulse can further be processed to quantify the flux and the energy of the radiation and other information about the radiation[1,5,6].Radiation detectors find applications in academic research, environmental safety, power regulation in nuclear reactors, personal protection of occupational workers, estimation of radiation dose in treatment of patients, calibration of radioactive isotopes among various other uses[7,8]. While radiation detection technology has evolved to address these scientific and industrial applications, world events have created new challenges and demands on radiation-detection technology for non-proliferation and national security applications, and new materials are needed to meet these challenges[9-12].

Neutral particles like neutrons are very difficult to detect because of the absence of any columbic interaction and limited interaction with the matter. A large number of applications require detection of neutrons which include nuclear medicine, high-energy physics, non-proliferation of special nuclear materials (SNM), astrophysics, structural biology and chemistry, magnetism and nuclear energy[13,14]. However, thermal neutron detectors have seen only incremental improvements in the last few decades and the gas based detectors (<sup>3</sup>He and BF<sub>3</sub>) are still widely used for the most of these applications with <sup>3</sup>He filled proportional counters being the gold standard for all future detectors[15]. Moreover these gas filled detectors are not the ideal detectors and while BF<sub>3</sub> is corrosive and toxic, the shortage of <sup>3</sup>He gas has made it prohibitively expensive[16-18 ]. The development of spallation neutron sources has increased the demand of thermal neutron detectors having higher efficiency and better radiation hardness. Hence, there is a strong need to explore alternative methods of thermal neutron detection [19,20]. Among various options the solid state detectors based on inorganic scintillators could provide a good choice with higher detection efficiency due to large density of neutron absorbing nuclei. These detectors can be portable, rugged and can operate at lower voltages when coupled with the advance silicon based photo sensors[21-23].

#### **1.2 Interaction of neutron with matter and their classification**

Neutron among all the ionizing radiations has always been the elusive particle since its discovery by Sir James Chadwick in 1932 owing to its neutral nature and the limited

interaction. The neutrons are stable within the nuclear dimensions in the quantized/bound energy states and could be generated in unbound form in a variety of nuclear interactions. Unlike quantized neutrons, free neutrons exhibit a half life of around 10 minutes[1, 24] and decay via beta emission  $[({}^{1}_{0}n \rightarrow {}^{1}_{1}p + {}^{0}_{-1}e + {}^{0}_{0}\nu)][11, 25]$ . The lack of Columbic interaction limits the interaction of free neutrons with the medium to the processes mainly classified as scattering and absorption. The result of these interactions is the emission of secondary radiations in the form of either charged particles or gamma radiation which are generated either because of neutron induced nuclear reaction or from the absorption of neutron by the target nuclei. These secondary radiations generating from the neutron interaction with the medium, creates the ionization in the medium of interaction and provide indirect signatures of neutrons[26, 27]. Most of the detectors utilize this type of conversion processes for the neutron detection. The relative probability of the neutron interactions is mainly governed by the neutron energy. From the detector point of view the neutrons can be classified grossly into two broad categories namely "slow neutrons" and "fast neutrons". The boundary energy of 0.5 eV corresponds to the cadmium cut-off energy where <sup>113</sup>Cd absorbs neutrons with high selectivity[28]. The neutrons with energy below 0.5eV are absorbed whereas those with energies higher than 0.5eV are transmitted. Slow neutron interactions include elastic scattering with the target nuclei with a large set of neutrons induced nuclear reactions. The small energy of neutron allows a very small energy transfer to the target nuclei, however results in further slowing down of neutron to thermal energies. Much of the population of thermal neutrons will be found with average energies of around 0.025 eV. These slow neutrons further initiate the neutron induced nuclear reactions with a positive 'Q' value for some atoms which are important for the detectors. The probability of the neutron induced reactions sharply falls off with the increase in neutron energy and the scattering becomes predominant[29]. Since the energetic neutron transfers a significant amount of energy to the

target nuclei, the radiation is now mostly due to the recoil nuclei. However, if the energy of the neutron is sufficiently high, inelastic scattering takes place and the target nucleus is elevated to one of the excited states. The target nuclei come to the ground state, subsequently followed by the emission of gamma radiation. The probability of neutron interaction for a given medium and interaction mechanism depends upon neutron energy and is expressed in terms of the microscopic cross- section ( $\sigma$ ) for each nucleus and the type of interaction. The probability for a certain nuclear process to take place can be measured in units of barns (1 barn =  $10^{-28}$  m<sup>2</sup>). The microscopic cross-section multiplied with the number of nuclei per unit volume turns into macroscopic cross-section ( $\Sigma = N\sigma$ ) which has the dimensions of inverse of the length. It basically represents the probability per unit path length for the specific process described by the microscopic cross-section ( $\sigma$ ). The total cross-section ( $\Sigma_{Tot}$ ) is the sum of all possible individual interactions.



Figure 1.1: Neutrons capture cross section Vs energy of neutron for few nuclei of interest for thermal neutron detection. energy as a function of radius of nuclei

The neutron mean free-path ( $\lambda$ ) is represented by  $\frac{1}{\Sigma_{Tot}}$  which is analogues to the gamma interaction. In solids, the mean free-path for slow neutrons falls in the order of centimeters whereas for fast neutrons it may go up to tens of centimeters due to weak interaction of fast neutrons with the medium. The cross-section for some important nuclei used for the neutron detection has been presented as a function of neutron energy as shown in Fig.1.1. It shows a decrease in the cross-section with increasing neutron energy. Further, there are various modes of interaction of neutrons with the medium whose probability depends upon the neutron energy and one or a combination of processes are more probably at a particular neutron energy. Since the type of reaction and its probability depend upon the medium as well the neutron energy, the neutrons are generally classified as per their energies as shown in the Table1.1.

Neutron classification	Neutron energy
Cold Neutrons	< 0.025eV
Thermal	0.025 eV (most probable energy at RT)
Slow	0.025 eV< E <1 eV
Fast	10 keV< E < 1 MeV
Fission	E > few MeV

Table 1.1: Classification of neutrons

Scattering and the absorption are two major processes by which the neutron interacts with a medium. The scattering can be further classified as elastic and inelastic in which the neutron transfers a part of its kinetic energy to the target nuclei and the total kinetic energy may or may not be conserved depending upon the nature of collision. However, in each case the result is a decrease in the energy of the incident neutron along with the ionisation produced

by the recoiling nuclei. Materials such as water, paraffin, plastic and graphite slow down the neutrons by elastic scattering and hence commonly used as moderators for thermalizing the neutrons[30]. The Fig.1.2 summarises the interaction of neutron with a medium.



Figure 1.2: Various modes of interaction of neutron with matter/nuclei

$$Total Cross - Section \Sigma = N\sigma$$
(1.2)

While elastic scattering is probable at all energies and for all nuclei, inelastic scattering does not occur below a certain threshold of energy which is the minimum energy required to excite the target nuclei. The fate of a high energy neutron has been shown in Fig.1.3 and explains all the processes that a neutron undergoes before being finally captured by a nucleus. It shows a neutron in an energy range of MeV undergoes several scattering processes until it comes to thermal energies at which it is finally absorbed by certain nuclei followed by the emission of fast neutrons and the cycle continues.


Figure 1.3: Fate of a high energy neutron while interacting with matter until it gets absorbed

### **1.3 General properties of Radiation Detectors and Scintillators**

A radiation detector is in general a device which can respond to the radiation interaction by inducing some ionized charge within the detector volume or produces some photons. It carries the signature of the nature, energy and the position of the radiation that has interacted with the detector medium. Ideally, the amount of charge produced or the number of photons released should be proportional to the energy of the incident radiation. The detector should also be able to transport the charges/photons produced to the further processing channel. Typically the collection time of the charges/photons by the detector for further processing varies from nanoseconds to milliseconds and is inherent property of the detector material. An ideal radiation detector should have following properties[31,32];

- High detection efficiency
- High-speed counting and timing ability (Counters and PET)
- Good energy resolution (Spectrometers)
- Linearity of response
- Detection of all types of particles and radiations
- Detection range to a wide energy range
- Discrimination between types of particles/radiation
- ✤ Low intrinsic background
- High spatial resolution (Imaging systems)

Although no single radiation detector material can have all these properties in common, hence the quest for the search of an ideal detector continues. As far as the operational mode of the radiation detectors are concerned, they can be operated in either the pulse mode, current mode or mean square voltage mode. In the pulse mode, a detector measures each individual quantum of radiation that interacts with the detector. This is achieved by the time integral of each burst of current or the total charge recorded by the detector as the total charge carriers produced is ideally directly proportional to the energy deposited in the detector by the incoming radiation. Pulse mode is required for counting, spectroscopic and imaging applications. In current mode, the detector measures the average rate of interaction by measuring the total current produced in the detector. Current mode is usually used in high flux events to avoid dead time losses. Based on their physical form factor, detectors can be classified as gaseous detectors, semiconductor detectors, organic scintillators and inorganic scintillators. Among all these detectors scintillators find a special place owing to their capabilities and suitability to wide range of applications. A scintillator is a material which produces light (mostly in the visible or UV range) when exposed to an ionizing event. Scintillators have gained a lot of attention over the last few years among other kind of detectors due to the advantages which include, the portability, ruggedness, fast response, ability to differentiate the type of radiation and the high detection efficiency to name a few. Scintillators in fact have been at the core of the nuclear, medical and industrial imaging in the last decade. Apart from that they find various applications in the field of high energy physics, spectroscopy and homeland security as well. The ability of a scintillator to distinguish between the different types of radiation with a relative ease and quantify its energy makes the use of scintillators more frequent than other types of detectors. A more detailed possible classification[33] has been shown in the Fig. 1.4.



Figure 1.4: Classification of Radiation Detectors

### **<u>1.4Thermal neutron detectors</u>**

Detectors for thermal neutrons rely on the nuclear reactions that result in prompt energetic charged particles to excite the charge carrier as a signature of neutron interaction with the detector. The cross-section for the thermal neutrons absorption depends upon the energy of neutron and the target nuclei. Hence virtually each type of neutron detectors involves the combination of target material designed to carry out the one of these underlying nuclear processes for detecting neutrons. The Table 2 presents the interaction of neutrons with some of the nuclei with higher capture cross-section for thermal neutron.

### **Table 1.2: Interaction of thermal neutrons**

Thermal neutron detectors can be classified as gas filled detectors, semiconductor detectors and scintillation detectors.

### **<u>1.4.1 Gas filled detectors</u>**

Gas filled detectors are among the first detectors used for the radiation detection. It consists of a nuclide having large cross-section for thermal neutrons to induce the secondary charge carriers. Commonly used gases for the thermal neutron detectors are  ${}^{3}$ He and BF<sub>3</sub> gases due to their high capture cross-section.

### <sup>3</sup>He Proportional counters

Pure <sup>3</sup>He is used as the conversion material in these gas filled detectors owing to their large cross-section (~ 5330 barns) for the  ${}^{3}$ He(n, p) ${}^{3}$ H reaction. The cross-section falls off with the increasing energy and drops to only 1 barn at a neutron energy of 1 MeV. The reaction probable with slow neutrons yields the 'Q' value of approx 765 keV with protons carrying an energy of 574 keV approximately while the tritium (<sup>3</sup>H) carrying nearly 191 keV of the energy. Although in gas form they are relatively insensitive to gamma radiation owing to the low density, they can be further discriminated from neutron signal due to their large difference in the amplitude of the signal. Helium-3 detectors generally can be operated at high pressures in the range from 0.2atm. to 10atm. and for a given gas pressure the detection efficiencies is proportional to its length[34]. The sensitivity of He-3 detectors increases with the pressure of He-3 gas. The detectors are usually operated in the voltage range from +1200 to 1800 Volts[35]. A major problem associated with the Helium-3 detectors is the wall effect resulting in a lower pulse height in the form of a plateau region near the full energy peak in the pulseheight spectrum. This arises due to some energy lost by the reaction products  $[^{3}He(n, p)^{3}H]$  in the interaction of neutrons with the helium-3. However, the supply of Helium-3 is limited due to the large half-life of tritium (12.3 years approx) which is its main source of production[36].

### **BF**<sub>3</sub>Proportional counters

This detector contains  $BF_3$  gas which serves the purpose of the target as well as the medium where the charged particle generated in the reaction can deposit their energy. The interaction of Boron-10 with neutron is listed in the Table 1.2. The natural isotopic ratio of <sup>10</sup>B is

approximately 20% in the compound. Similar to other proportional counters, it is fabricated in a cylindrical geometry where outer tube acts as the cathode while anode is the central wire in the detector. The typical neutron detection efficiencies for neutron energies close to thermal energies (0.025 eV) could be as high as 91 % for a 30 cm long tube containing the gas at a pressure of about 600 torr. But for the neutron energies above 100eV the efficiency drops to as low as 3.8%[37]. The operating voltages for these detectors are in the range from +1400 to 2800 Volts. To avoid the common wall effect in these gas based detectors, the BF<sub>3</sub> tubes are generally constructed with large dimensions so that the reactions products occur at a large distance from the detector's walls. The BF<sub>3</sub> detector has a lower sensitivity as compared to the <sup>3</sup>He detector to discriminate comparatively higher gamma background. The BF<sub>3</sub> detectors used in a gamma background up to 100mR/hr are well suited for measuring neutrons in mixed waste[38].

### 1.4.2 Semiconductor detectors

Standard device semiconductors like Si, Ge, CZT etc. do not contain enough neutron-absorbing nuclei to give reasonable neutron detection efficiency. Hence they are coated with a layer of neutron reactive material deposited on the surface of the detector to produce the charge carriers within the semiconductor. <sup>10</sup>B and <sup>6</sup>LiF are frequently used as the conversion layer materials because of their stability, large thermal neutron cross-sections, and primary reaction products. The charged particles created through the reaction of <sup>6</sup>Li and <sup>10</sup>B with the neutrons travel into the semiconductor material where they create electron-hole (e-h) pairs. The semiconductor detectors are operated under reverse bias and the electron-hole pairs generated within the semiconductor are separated by an externally applied electric field and are finally collected at the contacts. Generally a p-i-n diode configuration is used in place of the p-n junction to

enhance the charge collection efficiency and response time of the semiconductor based detectors. In order to ensure that the charged particles created in the neutron absorption travel to the semiconductor in order to produce the electron-hole pairs, a compromise of the thickness is made which limits their efficiency consequently. Apart from that the efficiency is also limited by the fact that only one charged particle among the reaction products which usually travels in the opposite direction due to the conservation of momentum can reach to the semiconductor. These difficulties have been overcome in recent 3-D semiconductor detectors where both the diode and conversion material dimensions are important design parameters and predict a theoretical efficiency in the range of 75% for the thermal neutron detection[39].

#### **<u>1.43 Scintillator detectors</u>**

Scintillation detectors include liquid organic scintillators, single crystals, plastics, glasses and fibres.

### Liquid organic scintillators.

These types of detectors are traditionally used for the fast neutrons detection where application area is very large and pulse shape discrimination is required to suppress the gamma background. A low thermal neutron detection efficiency and radiation damage effects are some of the drawbacks associated with these detectors.

### <sup>6</sup>Li-loaded glass fibers.

These detectors contain glass fibers loaded with <sup>6</sup>Li and doped with cerium. They have an advantage of large sensitivities and short decay times which are most suitable for high counting applications. However, relatively poor neutron and gamma discriminations are some of the drawbacks associated with these devices.

### <sup>6</sup>LiF/ZnS (Ag) scintillators:

The <sup>6</sup>Li acts as the neutron absorber while the ZnS (Ag) is a well-known phosphor used to detect the secondary charged particles produced in the reaction of <sup>6</sup>Li with neutrons. It offers high neutron detection efficiency and can be easily scaled up for large area applications. Discrimination of gamma background is not as good as compared to gas detectors.

#### Single crystal scintillators:

Scintillators in single crystal form offer various advantages compared to gas based and semiconductors based detectors. They are compact in size, offer higher efficiencies and are transparent to the emitted light for an efficient collection. They can be doped with suitable activators for fast counting applications. Mechanical and radiation hardness and reproducibility and reliability of results are some of the added perks associated with them. However, the limited interaction of neutrons leaves with a limited choice of materials that can be grown in single crystal form for the detection of thermal neutrons. The discrimination of neutrons and gamma radiation is though a big challenge with single crystal scintillators. Most of the single crystal scintillators use interactions of boron-10 (<sup>10</sup>B) and lithium-6 (<sup>6</sup>Li) with the thermal neutrons for the detection mechanism. It releases high Q value of energy and the low effective atomic number is beneficial in setting a discrimination level for gamma radiation background. Europium doped lithium iodide single crystals are the most widely used scintillator for thermal neutron detector but is flagged with the problems like hygroscopic nature and slow decay. Another class of materials are the elpasolites, a large family of halide scintillators that have recently attracted considerable interest for radiation detection. One of the materials from this family is Ce-doped Cs<sub>2</sub>LiYCl<sub>6</sub> (CLYC) which has shown capabilities to discriminate gamma and neutrons using pulse shape discrimination. CLYC also exhibits a good energy resolution, better than that of NaI(Tl), and as good as 4.3% at 662 keV[40]. However, these materials are highly hygroscopic and are difficult to make large size detectors due to crystal growth problems. Recently a class of borates containing <sup>6</sup>Li has also been explored in order to search for the thermal neutron detectors with large sensitivities. These constituent elements (<sup>6</sup>Li and? What to write <sup>10</sup>B) that possess a large thermal neutron capture cross-section and produce highly exothermic reactions. These materials also offer a large band gap to accommodate suitable dopants like cerium to offer fast action and good light-yield[41-44].

This thesis presents the work on scintillator materials for thermal neutron detection and hence the scintillation principle has been extensively discussed further.

### 1.4.3.1 Stages in Scintillation mechanism

The scintillation process consists of absorption of the incident energy, and conversion of it into the UV or Visible photons. A general overview of the overall scintillation process has been discussed below;

a) Absorption of radiation and generation of electron-hole (e-h pair) pairs:

The interaction of radiation with a medium leads to the generation of electron-hole pairs either directly in case of charged particles or electromagnetic photons. However, in case of neutrons the electron-hole pairs are generated through secondary processes consisting of either scattering or absorption processes.

b) <u>Relaxation of the charge carriers:</u>

The relaxation mechanism of the excite electron-hole pairs are different mainly due to the different migration mechanism owing to their masses. An excited electron can relax either radiatively by emitting a photon or it can release a secondary electron in a nonradiative process. The secondary electron emitted during this process is known as Auger electron which is released when an electron from the higher energy level fills up the hole. This auger electron can further create electron-hole pairs which can repeat the sequence of emission of radiative photon and the non radiative emission through Auger electron. Hence, this relaxation of the absorbed energy leads to a cascade of events of radiative and non-radiative transitions in the time range of  $10^{-13}$  to  $10^{-15}$ s[45].

### Thermalization of the energy deposited in the scintillator:

As the electrons migrate through the scintillator medium it loses its energy and when it becomes less than the ionization energy, the electron-phonon relaxation takes place due to lattice vibrations. This leads to the electrons moving down to the bottom of the conduction band while holes were being raised to the top level of the valence band. After the completion of the thermalization process, the energy of the e-h pair becomes equal to the energy corresponding to the band gap of the scintillator medium. Hence, the number of e-h pairs generated is proportional to the energy of the radiation.

### c) <u>Transfer of energy from e-h pairs to the luminescence centre:</u>

The migration of the e-h pairs through the lattice leads to the excitation of the electrons to the luminescence centres. There could be another mechanism of energy transfer where the excitons are self trapped at higher energy levels.

### d) <u>Emission from the luminescence centres:</u>

Luminescence can be classified as intrinsic and extrinsic. In case of an intrinsic luminescence the self trapped excitons are the energy carriers to the luminescence centres. On the other hand, the extrinsic luminescence takes place due to transitions in the dopant ion itself.

A brief schematic to the overall process discussed above is shown in Fig.1.5.



# Figure 1.5: Schematic diagram showing the scintillation process in an inorganic material

### **Desirable characteristics of Scintillators**

- a) High efficiency for conversion of excitation energy to fluorescent radiation
- b) Transparency to its fluorescent radiation
- c) Emission of light in a spectral range
- d) Detectable for the available photo sensors
- e) Short decay time to allow the fast response

### **1.5 Literature survey and material selection**

<sup>3</sup>He based gas detectors were the industry standard for thermal neutron detectors owing to their high efficiency and gamma discrimination[46]. However, the development of new materials and technologies based on photon detection has given scintillators an advantage over gas and semiconductors based detectors. While gas based detectors have limited efficiency due to lower

densities, they are not suitable for robust applications. On the other hand, semiconductors require low temperature operations to minimise dark current which leads to a poor pulse height discrimination. Hence the search for inorganic scintillators for thermal neutron detection have gained pace over the last decade due to development of new materials and the evolution of better and compact electronics. Most of these materials contain lithium and boron or combination of these in the lattice to increase the neutron interaction probability. In single crystal form they offer high detection efficiency, compactness and better mechanical and radiation hardness. While europium doped lithium iodide is a conventional thermal neutron detector[47], studies of lithium iodide doped with Tin, Silver and thallium have also been performed for thermal neutron detectors[47-50]. Some new inorganic scintillators which are currently being investigated are lithium rare-earth borate  $[(Li_6R(BO_3)_3) : R = Gd, Lu \& Y][51]$ and caesium lithium yttrium chloride [Cs<sub>2</sub>LiYCl<sub>6</sub>(CLYC)]. Single crystals of CLYC offer dual capabilities of both gamma and thermal neutron detection with the capabilities of discriminating the gamma pulses using the pulse-shape discrimination technique[52]. However, the material is highly hygroscopic which poses a major challenge during its crystal growth and long-term stability. On the other hand lithium rare-earth borates  $[(Li_6R(BO_3)_3) : R = Gd, Lu \& Y]$ are not hygroscopic and offer excellent optical properties which are suitable for scintillation applications [53-55]. This material was originally being explored as a laser host for applications as solid state lasers, though J.B. Czirr et al[53] reported, lithium gadolinium borates  $[Li_6Gd(BO_3)_3:]$ , as a potential candidate for scintillator for thermal neutron detection. This material contains <sup>6</sup>Li (natural abundance 7.4%,  $\sigma_{abs} = 940$  barns) and <sup>10</sup>B (natural abundance 20%,  $\sigma_{abs}$  = 3835 barns) that have large cross-sections for thermal neutrons and produce charged particles ( $\alpha$  and  ${}_{1}^{3}H$ ) after interaction[1,53-57]. The alpha particles generated in  ${}^{10}B$  (n,  $\alpha$ ) <sup>7</sup>Li and <sup>6</sup>Li (n,  $\alpha$ ) <sup>3</sup>H reactions excite the Ce<sup>3+</sup> ions resulting in an efficient emission at 420 nm which matches well with the efficiency response of bialkali photomultiplier tubes(PMT). A

large number of atoms in the unit cell provide higher probability for neutron interaction which can yield a higher efficiency for thermal neutron detection while a lower effective Z of the materials also helps transparency to gamma radiations[58,59]. J.B.Czirr et al [53], synthesized Li<sub>6</sub>Gd(BO<sub>3</sub>)<sub>3</sub> from the consentient oxides using solid state sintering in the 1990s. They carried out the optical and electronic studies on the as-grown single crystals. They used natural isotopic ratio of <sup>6</sup>Li and <sup>10</sup>B for the growth of single crystals. The single crystals were grown by the Czochralski technique using a resistive heating furnace which offers limited axial gradient. They compared the scintillation results with GS-20 and reported the pulse-height spectrum of  $Li_6Gd(BO_3)_3$  to be greater than GS-20[60]. Chaminade et al. [61] studied  $Li_6R(BO_3)_3$  system by using yttrium and gadolinium as rare-earth ions in the LRBO matrix. Cerium doped single crystals of LRBO were also grown using the Czochralski technique from their melts. They grew the single crystals in a conical vitreous carbon crucible in dried deoxygenated pure argon ambient[61]. The optimum pulling rate was in the range of 0.3-0.5 mm/h while the rotation rate was kept in the range of 5-7 rpm. The authors reported that as the amount of cerium increases due to segregation coefficient of cerium being less than 1 in the matrix the excess cerium is rejected into the melt[61]. This causes the rejected cerium to remain near the solid liquid interface. They reported the cerium doped LYBO to have a fast decay with a decay time around 28 ns. Their results on LGBO were consistent with the findings of J.B. Czirr et al [53] and he reported the LGBO to be 6 times more efficient than lithium glass scintillator. In 2002 Shekhovtsov also reported the growth of single crystals of Li<sub>6</sub>Gd(BO<sub>3</sub>)<sub>3</sub> from their melts using the Czochralski technique[62]. He grew single crystals along an oriented seed in air-ambient. He performed scintillation testing and described LGBO as promising scintillator for the thermal neutron detection. Later works of Chaminade et al. described the growth complications including the spiral growth of Li<sub>6</sub>Gd(BO<sub>3</sub>)<sub>3</sub>. Few authors concluded the spiral growth nature to instabilities of the surface tension due to the selective evaporations of the constituent

oxides [63]. Several attempts were made to minimize the spiral growing nature of  $Li_6Gd(BO_3)_3$ using lower rotation rates but were found to be insufficient. They also reported the highviscosity of the melt being the reason for the thermal instabilities in the melt [64]. Sablayrolls et al. explored  $Li_6Y(BO_3)_3$  in 2005 as a laser host material [65]. The growth of single crystals using the Czochralski technique in air was reported by these authors. They reported the optimized rotation in the range of 5-7 rpm and the pulling rate was 0.5mm per hour. Several other authors including, Rekia Belhoucif etal[66] and Yavetskiy et al. [125] did their studies on europium doped Li<sub>6</sub>Gd(BO<sub>3</sub>)<sub>3</sub> for laser applications. Several authors reported cracking in the grown crystals and concluded an orientation of [4 -3 2] to be necessary for the growth of crackfree single crystals[67]. J. Chen et al. [68] and few others also grew single crystal of Li<sub>6</sub>Gd(BO<sub>3</sub>)<sub>3</sub> using the Bridgeman technique and characterized the grown crystals using the photoluminescence. They reported the cracking of the crystals to be a major issue even though the starting charge for the growth consisted of a single phase material [61, 66-68]. Other similar crystal growth reports which include Brenier et al. who successfully carried out the growth of Li<sub>6</sub>YbY(BO<sub>3</sub>)<sub>3</sub> using the Czochralski technique under nitrogen ambient [69]. Zhao et al. obtained single crystals doped with erbium from the starting charge synthesized from a stoichiometric mixture of constituent oxides using the Czochralski technique. They reported the optical properties of these single crystals to be of high quality [70].

### **1.6 Scope and Aim of research**

The single crystal growth of the rare-earth borates have been discussed in the literature but have been flagged with a number of problems. Formation of single phase material, presence of bubbles and inclusions, large super-cooling and cracking due to the presence of cleavage planes are some of the associated problems with these group of materials. Although in all the works reported in literature so far has indicated the potential of these materials to detect thermal neutrons, the work done in this regard for development of thermal neutron detectors is limited. It was realised that a comprehensive effort is needed from the crystal growth to the scintillation characterization which could make a base for the development of detectors for the thermal neutron detection. Finally, the performance characteristics of the developed neutron detectors based on scintillators grown in this work was planned to compare with other conventional thermal neutron detectors. Hence the scope of this thesis is to optimise the crystal growth parameters for the growth of detector grade single crystal for thermal neutron detection. The activator concentration has been optimized to achieve the best light output possible from the material. The role of rare-earth ions (Gd, Lu and Y) in the host matrix has been investigated to understand the effect of these ions over the performance of the material. A real time study of the thermal neutron detection has been carried out using the scintillators processed from the crystals grown under optimized parameters. Finally, a portable thermal neutron detector has been developed to make the potential use of these detectors in nuclear industry.

# **CHAPTER2**

# **Experimental procedure**

# 2.1 Single crystal growth: Theory and techniques

The single crystal technology is a vital pillar of all the recent technologies and modern scientific development. It plays an important role in the area of immense technological excellence in the important areas of service to the humanity, medicine, engineering, technology and also strategic areas of defense and space science [71]. It is one of the most vital and significant field of material science which involves the controlled phase transformation of a fluid into a crystalline solid phase and the processing of the grown single crystal as per the requirement. The new solid state and the single crystals evolution mainly started with the invention of the transistor in 1948. Many new crystals have been grown since then and fabricated in order to assess the device properties. The application of semiconductors based on the electronics created an enormous demand for high quality of semiconductor, ferroelectric, piezoelectric, oxide etc. single crystal [71].

Single crystal growth needs inter-disciplinary research and requires chemists, physicists and material scientists to collaborate to develop the technology. The fundamental experimental aspects of the crystal growth were known since eighteenth century; however the real advancement in this field came after the development of thermodynamics in the late nineteenth century and with the development of nucleation and crystal growth theories. The methods for growing crystals are very vast and mainly dictated by the characteristics of the material and its size. A crystal growth is essentially a first order phase transition where a material can be transformed into the form of a single crystal by slow and gradual transformation from melt, solution or vapor phase[72]. During this phase transformation the atoms or molecules lose their random character gradually in uniform manner and achieve a long-range order in the form of crystalline solid. It is a two-step process where the nucleation of the single phase is followed by the addition of identical unit cells through mass transport which finally evolves into a big single grain with long range ordering on atomic scales. The transformation of the solid phase from the fluid takes place because of the change in free energy which is favorable only under certain conditions (Gibbs 1876, 1878) [73, 74]. The crystal growth is a complex process which involves optimization of various parameters such as temperature, pressure, chemical potential etc. and hence a comprehensive knowledge of the process is needed [75]. A large number of techniques can be employed based on the theoretical inputs for growing small crystal samples; from either of the melt, solution or vapor. The melt growth technique is still widely used for the growth of device grade single crystal. The various crystal growth techniques [76] have been listed in the Table 2.1 shown below.



# Table 2.1: List of techniques of crystal growth

The various methods used for the growth of single crystals according to their percentage use have been shown in the Fig. 2.1 below[77]. Nearly eighty percent of the single crystals are grown from melts worldwide due to the control that one can have over nucleation.



Figure 2.1: A pie chart showing percentage of crystals grown using various methods

# 2.1.1 Thermodynamics in Melt growth

The crystal growth is a non-equilibrium process where the control of the crystal growth environment and the growth kinetics, both at macroscopic and atomic levels are significant. The phase transformation during the crystal growth process is due to lowering of the free energy of the system. According to Gibbs expression, the free energy is related to entropy and internal energy as follows[78,79];

$$G = H - T \tag{2.1}$$

Where H stands for enthalpy, S represents entropy and T is the temperature. During the phase transformation which takes place at a constant temperature, the lowering of the free energy can be expressed as,

$$\Delta G = \Delta H - T\Delta \tag{2.2}$$

Where,

$$\Delta H = H_L - H_s \tag{2.3}$$

Where, (Subscript "L" stands for Liquid & "S" for Solid)

$$\Delta S = S_L - S_s \tag{2.4}$$

And

$$\Delta G = G_L - G_S \tag{2.5}$$

At equilibrium,  $\Delta G = 0$ , and therefore,

$$\Delta H = T_e * \Delta S \tag{2.6}$$

where Te is the equilibrium temperature. Hence,

$$\Delta G = \Delta H * \frac{\Delta T}{T_e}$$
, and  $\Delta T = T_e - T$  (2.7)

When  $T_e > T$ ,  $\Delta G$  is positive and depends upon the latent heat of transition. The free energy change can be expressed more conveniently as  $\Delta S * \Delta T$ , where  $\Delta T$  represents the super-cooling. Super-cooling is the state of the solution where it is brought below its melting point while still being in melt phase. This state is a highly unstable state which becomes the driving force for nucleation and further crystallization. Hence, a control over nucleation which can be achieved by the controlled super-cooling is a vital step in the crystal growth [80-81].

# **Nucleation**

Nucleation is the process of formation of a cluster of atoms or molecules to form the first nuclei or solid phase which will further lead to the crystal growth. This nucleation should be thermodynamically stable for the further crystal growth process to take place. For this the nuclei should grow to a critical size where the change in free energy due to all processes should be minimum. The stable formation of a nucleus involves three steps;

- a) The super-cooling of the melt
- b) Formation of the nucleus &
- c) Growth of nucleus to its critical size

Nucleation can be spontaneous or can be induced in presence of foreign surface and are classified as homogenous and heterogeneous nucleation. A homogenous nucleation is formed around the interior of the parent phase whereas nucleation around ions, impurity molecules or dust particles is referred as heterogeneous nucleation.

Now, the free energy change associated with the formation of a nucleus can be written as [82];

$$\Delta G = \Delta G_s + \Delta G_v \tag{2.8}$$

Where  $\Delta G_s$  is the excess surface free energy of the interface separating the parent and the product phases, and  $\Delta G_v$  is the volume excess free energy change per unit volume, which is a negative quantity. For a spherical nucleus of radius r,

$$\Delta G = 4\pi r^2 \sigma - \frac{4}{3}\pi r^3 \rho \Delta G_{\nu} \tag{2.9}$$

Where ' $\rho$ ' is the density of the liquid. The free energy of the system decreases by  $\Delta G_{\nu}$  for each unit volume of the solid created but increases by an equal amount to the interfacial energy, for each unit area of the solid-liquid interface formed [83,84]. A graphical representation of the expression discussed above has been shown in Fig.2.2 showing the contribution of the surface and the volume energy towards the free energy change of the system. The surface energy term increases as r<sup>2</sup> while the volume energy term decreases with r<sup>3</sup> and the net free energy change increases with increase in size until it attains a maximum after which it starts decreasing. The size of the nucleus corresponding to the maximum free energy change is known as the critical nucleus. This is the smallest size of the nucleus which stays stable and grows further and if the size of the nucleus is below the critical dimension then no further growth is possible and it redissociates in to the mother system[85].



Figure 2.2: Free energy curve for the surface free energy, volume free energy and total and total

The critical size of the nucleus may be obtained by taking the first derivative of the expression of  $\Delta G$  and setting up to zero. This leads to,

$$r^* = \frac{2\sigma}{\Delta G_{\nu}} \tag{2.10}$$

Substituting this value of  $r^*$  in equation (IV), the free energy change with the critical nuclei reduces to,

$$\Delta G = \frac{16\pi\sigma^3}{3\Delta G_v^2} \tag{2.11}$$

In general,

$$\Delta G = KTln(S). \qquad (2.12)$$

where "S" represents the degree of super cooling. Using above expression, the expression for the Gibbs free energy can be rewritten as

$$\Delta G = \frac{16\pi\sigma^3 \Omega^2}{3(KTlnS)^2} \tag{2.13}$$

Now, the rate of nucleation J, i.e. the number of nuclei formed per unit volume per unit time can be expressed by Arrhenius equation[86],

$$J = J_0 exp\left[\frac{-\Delta G^*}{KT}\right]$$
(2.14)

Substituting for  $\Delta G$  in the above expression gives,

$$J = J_0 exp \left[ \frac{-16\pi \sigma^3 \Omega^2}{3K^3 T^3 (lnS)^2} \right]$$
(2.15)

where  $J_0$  is the pre-exponential factor. This expression shows how the rate of nucleation is governed by the temperature T, degree of Super-cooling S and the interfacial energy  $\sigma$ . The above theoretical estimates gives a fair estimated about the nucleation process which takes place during the crystal growth from melts. The nuclei which grows and are thermodynamically stable may have different crystallographic orientation which may not be conductive for single crystal growth. Hence in order to grow a single crystal a single oriented nuclei is selected while melting all other into the system through a highly controlled environment which is created by selecting proper temperature profile, slow cooling rate (Homogenous nucleation), special crucible design or by initiating the growth through a single crystal seed (Heterogeneous nucleation). This is the basis for the most of the single crystal growth techniques which may use different mechanism to achieve this stage.

## 2.1.2 Single crystal growth techniques from melts

Single crystal growth from their melts is one of the most popular techniques for the growth of large size single crystals. It accounts for almost more than 80% of the growth that is carried out worldwide[87]. The main advantage of the technique lies in the convenience with which the parameters like temperature gradient, growth orientation, ambient and forced convection can be controlled. In principle, all the materials can be grown from their melts provided they melt congruently and do not undergo any phase transition between their melting point and the room temperature. The rate of growth is much higher than any another method and the process is relatively economical and is therefore one of the most prime reason for this method to be employed for the growth of commercial single crystals[88]. The melt growth can be carried out by the following techniques where the Czochralski is the most popular technique and has been discussed in detail.

- 1. Czochralski ("pulling")
- 2. Bridgman ("directional solidification")
- 3. Verneuil ("flame fusion")
- 4. Kyropoulos ("top seeding")
- 5. Laser-heated pedestal growth
- 6. Micro pulling
- 7. Floating Zone (including image furnace)

## 2.1.2.1 Czochralski Technique

The Czochralski process is named after Polish scientist Jan Czochralski who first used this method for the growth of some metal single crystals in 1918 [89]. It is basically a crystal pulling technique from the melt to produce high quality single crystals. This method is widely used for the growth of oxides such as sapphire, ruby and semiconductors. The entire semiconductor industry has evolved around the Czochralski growth technique which is used for the growth of silicon semiconductors. As a melt growth method, the primary condition is that the materials should have a congruent melting point. The major advantage of this technique lies in the growth rates [90, 91]. This method can be used over a large range of temperatures as long as a suitable material could be found for the crucible that can withstand those high temperatures. The disadvantages of this technique include strain in grown crystals, evaporation of constituents, and contamination of crucible material in the growth station between the heating coils. The heat losses due to conduction and radiation are minimised by using suitable

insulators in form of cylindrical tubes, wools and plates of various ceramics. The melting of the pre-synthesised starting charge is carried out using a RF or resistive heating element. Once the melting is achieved and thermalized, a seed crystal usually made of the same material attached to a pull rod made of re-crystallized alumina is brought in contact with the melt. The seed crystal is kept in contact with the melt for thermalization until a dynamic equilibrium is achieved. During this stage the melting and the crystallization of the molten material takes place over the seed material. The power of the heater is adjusted such that the rate of crystallization is controlled to ensure a single nucleation taking place. Once this stage is reached, the seed rod is pulled up at a very small rate which is mainly governed by the thermal conductivity of the material. It lies in the range of 0.2 mm/h to 0.5 mm/h for borates [92], 1-2 mm/h in case of some other oxides [93] while it goes in the range 5-10 mm/h in case of metals and semiconductor [94] single crystals. The pulled rate of the crystal and the power form the generator is varied in accordance to create a neck and a shoulder region in the growing crystal to minimise the defects and grow a cylindrical geometry to ensure uniform environment along the growing crystal. The growing crystal is continuously rotated to control the heat flows within the melt in order to stabilise the solid-melt interface for the defect free crystal growth. Finally the grown crystal is cooled down to room temperature with an optimum rate of cooling specific to the material.

# 2.1.2. 2 Crystal growth System

The assembly for growing the single crystal using Czochralski technique is usually called as "CZ Crystal Puller". It is equipped with a RF or Resistive heating power generator with control circuits and a weighing head to monitor the weight of the growing single crystal along with a pulling and rotation motor assembly used for the crystal pulling and continuous rotation of the growing crystal during the growth. The schematic of the CZ technique and the photograph of an automatic diameter control crystal puller are shown in the Fig. 2.3.



# Figure 2.3: Schematic of a typical Czochralski crystal growth system (L) and Crystal puller system [Cyberstar make Oxypuller] (R)

Further the weight of the growing crystal is continuously monitored and is compared with the reference growth rate based on the density, pull rate and the diameter of the growing crystal. The difference between the actual and the reference growth rate generates a feedback signal for the generator and PID (Proportional-Integral-derivative) control regulates the power through a closed loop feedback system in order to minimise the error signal. This helps in controlling the diameter of the growing crystal by regulating the power based on the feedback mechanism[95]. This is desirable to ensure the crystal grows in a uniform thermodynamic environment and has fewer defects that may be caused due to convective flows in the melt. This is achieved by a automatic diameter control (ADC) circuit/program. The schematic of the process is shown in the flow chart shown in Fig. 2.4. The growth of Lithium rare earth borates have been carried out in a cylindrical platinum crucible with flat bottom.



Figure 2.4: Schematic of a diameter control process in a Czochralski technique

The crucible was held fixed in a cylindrical ceramic tube of magnesia with zirconium wools wrap to provide the insulation and thermal stability. The axial temperature gradient has been adjusted between 60 K/cm to 120 K/cm just above the melt by employing passive after heaters and by adjusting the position of the crucible with respect to the induction coils [96]. The growth parameters (pull rate, rotation rate, temperature gradient, thermalization time, length of seed, shoulder and cylindrical region and cooling rate) were tuned by performing a series of experiments. Proportion and integration times were optimized based on the growth results to minimize the temperature oscillation occurring in the melt for the growth of defect free single crystals.

# 2.2 Differential thermal analysis

The differential thermal analysis is one of the most widely used tools to analyse the phase and the purity of the material. Apart from this it can also be used to sketch the phase diagram in a multi component system and can be used to perform the second order phase transitions studies as well in the material as a function of the temperature [97-99]. In this technique, the temperature of a sample is compared with that of an inert reference material during a programmed change of temperature. During an event of a phase change or reaction, the temperature of the sample changes which is compared with the reference and an equivalent current is flown in the sample furnace to maintain the temperature of the sample. This current is proportional to the enthalpy of the sample which is plotted against the temperature. This plot is usually referred as the DTA plot. The typical heating rate in DTA is usually 10k/min. The schematic of the DTA instrument has been shown in Fig. 2.5



# Figure 2.5: Block diagram showing the principle of the DTA measurement and a typical DTA plot

While a sample of mass m is heated, the sample receives energy and the internal energy of the sample changes with respect to the reference. This will lead to either a change in the phase of the sample or in the temperature. Without a phase transition, the amount of heat ( $\Delta Q$ ) received, is proportional to the change in temperature,  $\Delta T$  and is related to the expression given below.

$$\Delta Q = mC\Delta T \tag{2.16}$$

Where "C" is the specific heat capacity. The heat capacity depends upon the pressure and the thermodynamic condition under which the sample has been heated. Normally, the DTA experiments are carried out at a constant pressure and are related to the thermodynamic parameters as given in equation below.

$$C_{p} - C_{v} = T \left(\frac{\partial V}{\partial T}\right)_{p} \left(\frac{\partial P}{\partial T}\right)_{v}$$
 (2.17)

Where  $C_p$  and  $C_v$  are the specific heat at constant pressure and constant volume respectively. Another important state variable, the enthalpy can be defined as,

$$H = U + PV \tag{2.18}$$

Where "U" is the internal energy, "P" represents pressure while the "V" stands for volume.

Further,

$$C_{\rm p} = \left(\frac{\partial H}{\partial T}\right)_{\rm p} \tag{2.19}$$

Hence, the change in enthalpy can be obtained by integrating the function between the two temperatures.

$$\Delta H = \int_{T_1}^{T_2} C_p \, \mathrm{d}T \tag{2.20}$$

where  $C_p$  itself is a function of temperature. The thermal transformation in the substance creates a change in the enthalpy. During the continuous heating of the substance, the temperature reaches a value  $T_u$  after which stays constant during phase change and then changes again. Hence,

$$\Delta H = \int_{T_1}^{T_u} C_p \, dT + \, \Delta H_u + \int_u^{T_2} C_p \, dT$$
 (2.21)

Now,

$$G = H - TS \tag{2.22}$$

Hence,

$$\left(\frac{\partial G}{\partial T}\right)_{\rm p} = -S, \left(\frac{\partial G}{\partial P}\right)_{\rm T} = V$$
 (2.23)

For a phase transition  $\alpha \rightarrow \beta$ , the expression for the chemical potential can be expressed as shown in equation 2.24 [100],

$$\left(\frac{\partial \mu_{\beta}}{\partial P}\right)_{T} - \left(\frac{\partial \mu_{\alpha}}{\partial P}\right)_{T} = \left(\frac{\partial \Delta \mu}{\partial P}\right)_{T} = \Delta V_{m} \neq 0 \qquad (2.24)$$

And,

$$\left(\frac{\partial\mu_{\beta}}{\partial T}\right)_{P} - \left(\frac{\partial\mu_{\alpha}}{\partial T}\right)_{P} = \left(\frac{\partial\Delta\mu}{\partial T}\right)_{P} = -\Delta SV_{m} = -\frac{\Delta H_{m}}{T} \neq 0 \qquad (2.25)$$

Now, if the first derivative of the chemical potential expressed here changes abruptly and is discontinues then it is classified as a first order phase transition. However, if the first order derivative of this chemical potential function is continuous and the second derivative has an abrupt change then it falls into the category of second order. The Fig.2.6 shows a typical plot of DTA for the first and the second order transitions.



Figure 2.6: A typical heat flow pattern during the heating and cooling sequence of a single phase material

# 2.3 X-Ray diffraction

The material properties can be assigned to the arrangement of atoms in its crystal structure. Xray diffraction (XRD) is a powerful non-destructive technique for characterizing the crystalline materials. It provides information on crystal structure, phase, preferred crystal orientation (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects [101].

Crystal structure contains layers or plane of ions in a lattice cage where the separation between the crystal planes are in the order of the X ray wavelength. This results in the diffraction of X-rays when a beam of X-rays falls on a crystalline system and is usually referred as Bragg's reflection. X-ray diffraction peaks are produced by constructive interference of a monochromatic beam of X-rays diffracted at specific angles from each set of lattice planes in a sample. The intensity of the diffracted beam depends upon the distribution of atoms within the lattice and the electron cloud related to them[102].Fig. 2.7 shows the Bragg reflections from a crystal lattice plane. The X-ray pattern can be regarded as a DNA finger print of the material which is specific to a given phase and hence a data base is maintained which can be matched with the sample's XRD plot to identify the phase of the substance. Analysis of the diffraction pattern allows the identification of phases within a given sample. It is also possible to quantify each phase present, the crystallinity of a sample, the crystal structures and their lattice parameters, crystallite size and strain with the XRD pattern [103].



Figure 2.7: Bragg's law of X-ray diffraction

# 2.3.1 Powder X-Ray diffraction

The power XRD technique relies on the fact that in a polycrystalline sample there are enough crystallites with roughly all possible orientation such that the X-ray reflections corresponding to the all possible crystal planes can be recorded. This helps to achieve a signature pattern for the material which has enough reflections to virtually find out our phase from any number of the crystalline phases present. The power XRD pattern is capable of differentiating among crystalline and amorphous phases [104,105]. A schematic of a power XRD set up is shown in Fig. 2.8 below.



Figure 2.8: Schematic of an X-ray powder diffractometer

# 2.3.2 Single crystal X-Ray diffraction

Single crystal XRD is a versatile technique in true sense as it can be used to determine the crystal system, space group, atom locations, bond types, bond locations, bond angles, chemical content of unit cell without needing any data base. As in this case the Bragg angle is fixed for every set of planes in the crystal, each set of planes diffracts a particular wavelength from the white radiation that satisfies the Bragg's law for the values of d and  $\theta$  involved. Each point therefore corresponds to a different set of planes. These reflections generate a unique pattern for a particular orientation that is used to identify the crystal orientation[106]. Beam which are diffracted in a backward direction are recorded on a photographic film placed in reflection method. Fig.2.9: shows the schematics of Laue back reflection method.



Figure 2.9: Schematics of Laue back reflection method

# 2.3.3 High Resolution X Ray Diffraction (HRXRD)

Typical divergence of X-ray beam in powder XRD instrument is of the order of 500 arc seconds, whereas the actual spread of the diffraction peak of a good crystal is just a few arc seconds. The measurements of true diffraction peak width of a single crystal, therefore requires high resolution XRD (HR-XRD) where the divergence and wavelength spread of incident and diffracted X-ray beam is limited through Beam conditioners (comprising of crystal monochromators and slits) to get collimated and monochromatic beam [107]. Movement in different directions, tilt and rotation of sample stage help in precise placement of sample. Fig. 2.10 shows a schematic diagram of a triple-axis HRXRD instrument. Structural perfection of a single crystal can be determined by recording the rocking curve where a well collimated X-ray beam incident on the crystallographic plane of the sample being rocked by just few degree. Spread of the peak recorded for the diffracted beam is a measure of the degree of strain in the lattice.



Figure 2.10: Schematic diagram of a HRXRD measurement procedure

# **2.4 Optical Transmission**

Transmission/absorption spectroscopy is a strong tool to observe optical quality as sample to probe the absorption levels introduced by dopant or impurities [108]. Optical transmission/absorption measurements are carried out on a spectrophotometer that measures intensity of light transmitted/absorbed through a sample with respect to a reference sample (in most cases air or vacuum). The ratio of the intensity of light passing through a sample (I), to that of light without passing through the sample (Io) is called the transmittance and is usually expressed as a percentage (%T). The absorbance, A, is related to the transmittance as

 $A = -\log(\% T / 100)$ 

The schematic diagram of a double beam UV/VIS spectrophotometer is shown in Fig.2.11. Here the light is split into two beams before it reaches the sample. One beam is used as the reference and the other beam passes through the sample.



Figure2.11: Schematic diagram of a double beam UV-VIS-NIR spectrophotometer.

Two separate detectors are used for the measurement of light passing through the sample and the reference. Generally, two lamps one deuterium lamp for UV and second tungsten lamp for VIS/NIR, are used to cover UV VIS-NIR range of the spectrum. Photomultiplier tube is used for UV/VIS (range 190-850nm) and cooled PbS detector is used for NIR (range 800-2500 nm) [109]. The measurements were carried out in the wavelength range from 200 nm to 1100 nm and samples were taken in the form of thick slices (2-20 mm) prepared from the transverse section of the grown crystals.

# 2.5.1 Photo-Luminescence (PL)

Luminescence is the phenomenon in which absorption of light of a given wavelength by a molecule is followed by the emission of light at longer wavelengths [110]. Different type of transitions that can occur between ground and excited states are shown in Fig. 2.12. Emission
spectrum is the distribution of wavelength-dependent intensity of emitted energy while the distribution of wavelength-dependent intensity that causes luminescence is known as the luminescence excitation spectrum. The electronic structure and dynamics of an excited state of a molecule may be elucidated from luminescence as it is a property related to the difference between two electronic states, viz. the emitting state and the ground state. The difference in the timing between the absorption of the higher energy photon and emission of secondary photon of lower energy is defined by the luminescence decay time or the lifetime of excitation states [111]. Decay time can vary many orders of magnitude for different materials. Based on practical observations of persistence of two types PL was historically called fluorescence for life times shorter than 100µs and much longer lasting up to a few hours and even days is called phosphorescence. The basic mechanism of luminescence has been shown in Fig.2.12. Based on the type of excitation mechanism, luminescence can be classified as photoluminescence, Radioluminescence, thermo-luminescence, electro-luminescence to name a few. Each one has a unique advantage as it explores different defect centers by understanding the emission from the luminescent centres as the de-excitation mechanism/path is different in each mode of excitation [111,112].



Figure 2.12: Schematic showing mechanism of luminescence in inorganic materials

The schematic of Edinburgh fluorescence[113] spectrometer model FLP 920 is shown in Fig.2.13. It consists of monochromator, sample chamber, emission monochromator and detector. Two types of excitation source viz. Xe or H<sub>2</sub> filled flash lamps were used for recording the life times in the range of  $\mu$ s and ns respectively. The lamp produces a broad spectrum of high intensity radiation through the UV-Vis-NIR range which is imaged onto the entrance slit of the excitation monochromator. A specific excitation wavelength with a specific bandwidth is selected by the monochromator and passed from an iris (so that the intensity can be controlled) and then focused onto the sample. A portion of any luminescence from the sample is collected by a lens system and focused onto the emission monochromator. The emission monochromator selects a wavelength and spectral bandwidth of this emission and the light is passed into a photomultiplier tube (PMT) for emission in UV-VIS range or into an InGaAs detector for emissions in the near IR region.



Figure 2.13: The schematic diagram of a fluorescence spectrometer FLP920

The lifetime measurement in this system is based on **Time Correlated Single Photon Counting (TCSPC)** technique [114]. The schematic of this technique is shown in Fig.2.14. TCSPC measures single photons – namely, detection at the quantum limit. The technique requires an excitation source with high repetitive pulse output. The method makes use of the fact that for low level, high repetition rate signals the light intensity is usually so low that the probability to detect one photon in one signal period is much less than one. As the process of capturing a single photon is repeated several thousand or even million times per second, a sufficiently high number of single photons are processed for the resulting fluorescence lifetime measurement. The TCSPC electronics can be compared to a fast stopwatch with two inputs. The clock is started by the START signal pulse and stopped by the STOP signal pulse.



Figure 2.14: A schematic sketch of a life time measurement set up

The time measured for one START – STOP sequence will be represented by an increase of a memory value in a histogram, in which the channels on the x-axis represent the time. With a high repetitive light source millions of START – STOP sequences can be measured in a short time. The resulting histogram counts versus channels will represent the fluorescence intensity versus time. Photoluminescence (PL) studies were performed over wavelength range of 300–800 nm and temperature range of 77–300K, employing Edinburg fluorescence spectrometer Model FLP920. The emission was recorded in the reflection geometry by positioning the samples at an angle of  $45^{\circ}$  to the excitation beam. For measurements in the spectral domain, a

150 W Xe are lamp was used as the excitation source and a spectral bandwidth of 1 nm was selected for both excitation and emission monochromators. A hydrogen gas filled flash lamp operating at a repetition rate of 40 kHz was employed for recording the temporal behaviour of the luminescence decay. Measurements at low-temperature were carried out by placing the sample in Oxford Cryostat Model Optistat DN. The recorded luminescence spectra were corrected for spectral sensitivity function of the instrument. The correction file was prepared by recording the spectra under identical conditions after replacing the sample by a scatterer. The luminescence measurements were also repeated with cleaved samples to rule out the effects of any surface contamination arising due to polishing.

#### 2.5.2 Radio-luminescence

**Radio-luminescence (RL)** is caused by exciting the material with high energy radiation like Xray, gamma-ray etc. which is followed by the creation of charge carrier and their relaxation at the luminescent centers[115]. The radio-luminescence is different from photoluminescence as in RL the electrons are excited deep in conduction band and the process of relaxation is relatively complex as compared to PL where only the band transitions occurs. The spectrum consists of the intensity distribution generated from the high energy radiation as a function of wavelength. The instrument consists of an X-ray source and a monochromator assembly to record the spectrum. A monochromator and its compatible software (make: Princeton Instruments Acton spectra pro SP-2300) along with a white X-ray source with Cu target has been used to record the radio-luminescence spectrum. For the excitation, the accelerating voltage was kept at 40kV and a tube current of 30 mA.

#### **2.6 Scintillation measurements:**

Scintillation Detectors: In this study scintillation detectors were fabricated using the grown single crystal to check their scintillation performance. A scintillator detector consists of

following components; A scintillator material: to convert the high energy radiation in to detectable light in proportional to the energy of the ionizing radiation; Photo-detector to detect the light produced in scintillator and generate a processable electrical signal proportional to the detected light (PMT, Photodiode etc); Preamplifier: to amplify the signal received from the photo-detector and give a voltage pulse; Shaping amplifier to shape the pulse received from the preamplifier and transfer it to the pulse height analyzer (0-10 Volts pulse); Pulse height analyzer: a multichannel analyzer that assigns a registered pulse a channel number (0-8191 for an 8k MCA) proportion to its voltage (0-10 Volts) [116]. Schematic of a typical scintillation detector has been shown in Fig. 2.15.



Figure 2.15: Schematic of a scintillator set up

# **CHAPTER 3**

# <u>Growth and Characterization of Li<sub>6</sub>Gd(BO<sub>3</sub>)<sub>3</sub></u>

## **3.1 Introduction to material**

The single crystals of lithium rare earth borates  $\text{Li}_6\text{R}(\text{BO}_3)_3$  [LRBO; R=Gd, Lu &Y)] doped with suitable activators have attracted the researchers the most among the family of borates due to their potential application as scintillators for the neutron detection [61,117]. The unit cell contains a large number of boron atoms (<sup>10</sup>B isotope) that yield an energy of approximately 2.8 MeV for the absorbed thermal neutron through the <sup>10</sup>B (n,  $\alpha$ ) <sup>7</sup>Li reaction. In addition, Li atoms allow the use of <sup>6</sup>Li (n,  $\alpha$ ) <sup>3</sup>H reaction to give an overall "Q" value of energy 4.8 MeV [118]. The large atomic density of neutron absorbing nuclei in these materials ensures better detection efficiency. This family of borates have a large band gap (E<sub>g</sub> ~ 8-9 eV) and allows the doping of several rare-earth ions to tailor its luminescent properties for applications including laser, scintillators, etc. [119]. Among these Ce doped LGBO (LGBO:Ce) is more promising as a scintillator for the neutron detection due to its short decay time (~27 ns) [120] and high light output yield which is approximately six fold that of <sup>6</sup>Li-glass scintillators currently used as neutron detectors [121,122].

The single crystal growth of large size doped LGBO single crystals has been reported to be complicated due to difficulties in obtaining a single phase raw material of the stoichiometric composition [123]. High vapour pressure of the constituent oxides near the melting temperature makes the melt more prone to polymerise and supercool which leads to the formation of metastable phases. Due to these problems the single crystal growth of this material is reported to be flagged with problems of cracking either during the growth or during cooling [100,124127]. In addition to the problems reported for the growth of LGBO:Ce crystals the excess formation of Ce<sup>4+</sup> (which is non-radiative) compared to the Ce<sup>3+</sup> ions in the LGBO crystal when grown in air ambient presents challenge in obtaining single crystals with desired properties [128]. The Bridgman techniques have also been also reported in literature to be employed to grow single crystals from their melts to address some of the growth related problems [68, 129]. However the growth of high quality, large size, crack-free LGBO:Ce crystal is only possible by using the Czochralski technique. It may be noted that the most of work reported has been carried out on the disc of very small size (around 5mm x 6mm x 1mm) crystals [118,119].

The LGBO crystallizes to a monoclinic lattice with  $P2_{1/C}$  space group with cell parameters; a=7.2 Å, b=16.5Å, c=6.7 Å and  $\beta=105.36^{\circ}$  [123,124,125]. Here, the Gdpolyhedra (co-ordinated with eight oxygen atoms) and Li-polyhedra (co-ordinated by 4 and 5 oxygen atoms) are coupled with each other by B-O triangles (B-O bond distance of 1.36-1.39 Å) to form a 3 dimensional framework. In the LGBO matrix the Gd ions forms a zigzag chain aligned along the (001) direction with Gd-Gd distance of 3.8 Å which is smaller than the interchain distance which is around 7Å [124]. Hence the interaction of the Gd ions along the chain are more probable over that of intra-chain ions in the LGBO crystal and are expected to influence its optical and luminescence properties. Fig.3.1 shows the crystal structure of a unit cell of LGBO:Ce.



Figure 3.1 : Crystal structure of a unit cell of Li<sub>6</sub>Gd(BO<sub>3</sub>)<sub>3</sub>:LGBO)

The luminescence and energy transfer mechanism of Ce doped LGBO crystals have been discussed by several authors and have indicated energy transfer between  $Gd^{3+}$  and the doped  $Ce^{3+}$  ion [130-132]. Although the resonant energy transfer from  $Gd^{3+}$  to  $Ce^{3+}$  and change in decay kinetics has been investigated in the past, most of the investigations have focused on the 400 nm emission of  $Ce^{3+}$ . The emission at 313 nm due to transitions in the  $Gd^{3+}$  which plays a major role in the energy transfer has not been studied in detail [119, 109, 133-136]. Hence a more detailed work is required to understand the energy transfer between  $Gd^{3+}$  and  $Ce^{3+}$  in LGBO:Ce and its dependence with the temperature. Single crystals of pure and cerium doped (0.1 mol % to 1 mol %) LGBO of 20 mm diameter and 30 mm length were grown using the Czochralski technique. Temperature dependence of photoluminescence measurements has been performed on these crystals from 77K to 300K to study the emission characteristics of the  $Ce^{3+}$  ions in the LGBO:Ce crystal at different wavelengths of excitation. A direct evidence of an

energy transfer occurring between  $Gd^{3+}$  and  $Ce^{3+}$  ions and its temperature dependence could be established by measuring the temperature dependence of emission intensity corresponding to  $Ce^{3+}$  and  $Gd^{3+}$  ions and their decay times respectively.

#### **3.2 Experimental Procedure**

The LGBO:Ce single crystals were grown along (010) direction using the Czochralski technique (Cyberstar make Oxypuller). The constituent oxides (Li<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>) with high purity (99.99%) were mixed in a stoichiometric ratio and were subjected to a two step solid state reaction process to prepare the starting charge for the growth of single crystals. The thoroughly mixed charge was heated at 750°C for 10 h in an alumina crucible which was followed by another sintering at 750°C for 24 h after crushing and through mixing of the charge sintered during the first stage. The two step sintering process was found to be essential as incomplete phase formation takes place in single stage sintering process. As prepared material was taken in a platinum crucible and heated to 900°C in 4 h in the air ambient for the single crystals growth of LGBO. The melt was kept for 2h at this temperature for better homogenization. A pull rate of 0.7 mm/h for undoped LGBO and 0.5 mm/h for LGBO:Ce crystals have been employed. The seed rotation rate was in the range of 12 to 15 rpm throughout the crystal growth. Powder XRD (Rigaku make RINT-2200) and Differential Thermal Analyser (SETRAM make DTA-TG 92) were performed on the starting charge as well as the samples from the grown crystals to verify the single phase. The high resolution XRD (HRXRD) was also recorded to determine the crystalline quality. Omega scan was carried out for the reflection from the (010) plane. Optical measurements were performed over 2 mm thick discs that were cut from the as-grown crystals and polished to mirror finish using alumina powders down to 0.3 µm size. A UV-Vis spectrophotometer JASCO (Model-V 670) has been used to record the transmission spectra in the wavelength range from 200 nm to 1100 nm. Photoluminescence studies were performed over a wavelength range from 200 - 500 nm in a temperature range of 77 - 300K employing a fluorescence spectrometer (Edinburg Model-FLP920). A cryostat (Oxford, Optistat-DN) was used for the low-temperature measurements. The emission was recorded in the reflection geometry mode by positioning the sample at  $45^{\circ}$  with respect to the excitation beam. A steady state xenon lamp was used as an excitation source and a spectral bandwidth of 1 nm was selected for both excitation and emission monochromators. The recorded luminescence spectra were corrected for the spectral sensitivity with the instrument response function. Fluorescence life time measurements were performed with a xenon flash lamp having a pulse width of 10 µs and a repetition frequency of 100 Hz.

## 3.3 Results and discussion

The photographs of the single crystals of undoped 0.1 %, 0.5 % and 1% Ce doped LGBO are shown in Fig.3.2. The grown crystals were transparent and crack free with dimensions up to 20 mm diameter and 30 mm length. The increase in concentration of the cerium has been found to be affecting the crystal growth characteristics beyond 1% of the molar concentration. It was also found that the crystals with higher cerium concentration were more prone to the cracking.



Initial crystal growth attempts



Undoped (L) and 0.1 % Ce doped (R)





0.5 % Ce doped

1 % Ce doped

Figure 3.2 : Photographs of as grown single crystals of Li<sub>6</sub>Gd(BO<sub>3</sub>)<sub>3</sub>

Fig.3.3 shows the DTA pattern of the as grown crystal. It shows a large supercooling of 150K and a very narrow temperature range (width < 1.5K) for the freezing of the melt. This lead to the problems in the crystallization of the melt in a transparent ingot and all the initial crystal growth experiments performed under low temperature gradient resulted in a polycrystalline growth. This problem was mainly arising due to the large freezing range and was overcome by employing a larger axial temperature gradient (nearly 60-70K/cm) just above the melt.



Figure 3.3: Melting and freezing behavior of LGBO

However, the crystals grown under higher temperature gradient were found to be cracked during the growth or cooling due to severe thermal stress generated during the growth. This thermal stress was minimized by employing a lower pull rate of about 0.8 mm/h for the undoped crystals while about 0.5 mm/h for the doped single crystals. Further the cooling rate of the crystal was also limited below 30°C/h to avoid cracking during cooling. The power XRD pattern of the LGBO:Ce material with indexing has been shown in Fig. 3.4. The graph in the inset shows the racking curve from the (010) plane of the LGBO single crystal. The Powder XRD pattern matches completely with the JCPDS card No. 80-0843 which confirmed the synthesis and growth of the single phase material [137].A symmetric rocking curve confirmed the crystal quality though the higher FWHM of about 175 arc-seconds suggests the strain

commonly present in high temperature growth. Post growth annealing is commonly used to further reduce the strain present during the growth of the single crystals [138].



Figure 3.4 : Powder XRD pattern of LGBO (Inset HRXRD of the peak corresponding to (010) plane)

The transmission spectrum of the undoped, 0.1% and 0.5% Cerium doped single crystals have been presented in Fig. 3.5. The spectrum of the undoped crystals shows sharp absorption lines below 350 nm corresponding to the various transitions of the Gd<sup>3+</sup> ions in the LGBO matrix. However, at concentrations above 0.5 mole percent the characteristic absorption lines due to gadolinium got merged in the continuous absorption band. This was consistent with the literature [128]. The electronic properties of the LGBO depend upon both the gadolinium and the cerium which have been further studied in detail using the photoluminescence measurement.



Figure 3.5 : Transmission spectra of undoped (red dotted line), 0.1% Ce doped (black solid line) single crystals of Li<sub>6</sub>Gd(BO<sub>3</sub>)<sub>3</sub> and 0.5 % Ce doped (blue dotted line)

The excitation and emission spectrum of the LGBO:Ce is shown in Fig. 3.6. The emission spectrum of LGBO:Ce at room temperature consists of two bands centred at 313 nm and 400 nm. The emission band at 400 nm corresponds to the Ce<sup>3+</sup> centers while that at 313 nm is arising from the Gd<sup>3+</sup> centers corresponding to the transition from  ${}^{6}P_{7/2} \rightarrow {}^{8}S_{7/2}$  [68, 139]. The excitation bands centred at 312 nm and 345 nm corresponding to the 400 nm emission are due to transitions within the Ce<sup>3+</sup> ions from the 4f level to the 5d level [140]. The 312 nm excitation band of Ce<sup>3+</sup> overlaps with the absorption bands of the Gd<sup>3+</sup> which lies at 301, 306 and 312 nm ( ${}^{8}S_{7/2} \rightarrow {}^{6}P_{J}$ ). This leads to non radiative transfer of the excitation energy from  ${}^{6}P_{7/2}$  of Gd<sup>3+</sup> to 5d levels of Ce<sup>3+</sup> ion (a simultaneous de-excitation of Gd<sup>3+</sup> and excitation of Ce<sup>3+</sup> centers) is a dominating process mainly due to large decay constant of the  ${}^{6}P_{7/2}$  state. The excitation band at 274 nm ( ${}^{8}S_{7/2} \rightarrow {}^{6}I_{J}$  of Gd<sup>3+</sup>) which corresponds to the 400 nm emission from the cerium centres

is due to the energy transfer from  $Gd^{3+}$  to  $Ce^{3+}$  centers [140,142,143]. The inset of figure 5 shows the excitation spectrum from LGBO:Ce corresponding to the emission at 313 nm from



Figure 3.6: Excitation (black dotted line) and emission (red solid line) spectra of Li<sub>6</sub>Gd(BO<sub>3</sub>)<sub>3</sub>:Ce crystal. (The excitation spectrum for emission at 313 nm is shown in the inset).

the  $Gd^{3+}(^{6}P_{J}\rightarrow ^{8}S_{7/2})$  and has excitation bands observed at 274, 250 and 247 nm. There is another excitation band at 312 nm corresponding to the emission at 313 nm with a very narrow stokes shift [68]. The energy level diagram has been drawn based on the excitation and emission spectrum to understand the electronic properties of the LGBO:Ce and is shown in Fig. 3.7.



Figure 3.7: Energy level schemes of Ce<sup>3+</sup> and Gd<sup>3+</sup> ions in the Li<sub>6</sub>Gd(BO<sub>3</sub>)<sub>3</sub> matrix.

The energy levels of the  $Ce^{3+}$  and  $Gd^{3+}$  have been drawn in the same scale and are assigned with the rare earth ions energy levels [139].

The low temperature PL measurements were performed over undoped and doped single crystals to understand the energy transfer mechanism in the LGBO:Ce matrix. The emission band at 313 nm recorded at a slit width of 0.05 nm in the emission arm is shown is Fig 3.8.



Figure 3.8:Emission spectra at 313 nm (solid circle) for the excitation at 274 nm. (Dashed green line- Individual gaussian fit



Figure 3.9 (b): Temperature map of  $Gd^{3+}$  emission at 313 nm for excitation at 274 nm for 0.1% Ce doped  $Li_6Gd(BO_3)_3$  single crystal



Figure 3.9 (a): Temperature map of Gd<sup>3+</sup> emission at 313 nm for excitation at 274 nm for undoped Li<sub>6</sub>Gd(BO<sub>3</sub>)<sub>3</sub> single crystal.



Figure 3.9 (c): Comparison of the temperature dependence (■- doped and □ -undoped) for undoped and doped single crystals cases.

It could deconvolute into three peaks and the temperature dependence of this emission band for the undoped and the cerium doped crystals has been shown in Fig. 3.9 (a) and Fig. 3.9 (b) respectively. In case of undoped LGBO, the intensity of this emission band at 313 nm increases monotonically with temperature. However, the cerium doped LGBO single crystals shows a strange behaviour where intensity increases till  $\sim 200$  K and then becomes stagnant for a while

to further increase again beyond temperature of 240 K respectively. This suggests some kind of activation energy required at  $\sim 200$  K for further increase of intensity with temperature. In order to understand the behaviour of the undoped and the doped LGBO, the integrated intensity has been plotted to compare the temperature dependence and is shown in Fig. 3.9 (c). The reason for this enhanced emission of Gd<sup>3+</sup> at 313 nm in undoped single crystals is the smaller intra chain distance (3.8 Å) between two Gd ions with respect to a larger inter-chain distance (6.5 Å) [125]. Hence there is a dominant interaction between the intra-chain  $Gd^{3+}$  which is due to the enhanced migration of electronic excitation energy along this chain that prevents the concentration quenching of the intrinsic luminescence of Gd<sup>3+</sup> ion (which is otherwise reported to be quenched in other matrices like  $Gd_2SiO_5$  [144]. However, in case of LGBO:Ce samples the intensity of the emission at 313 nm first increases slightly up to 200 K (but much lower compared with undoped samples), after that there is a sudden jump in intensity after which it increases monotonically once again. This may possibly be due to presence of Ce<sup>3+</sup> ions in the LGBO:Ce that replaces the Gd<sup>3+</sup> ions and breaks the Gd-Gd chain and produces a potential barrier which hinders in the migration of electronic energy. This barrier was found to be overcome at ~ 190 K (by thermal energy) giving a sudden jump in the integrated intensity of this emission band at 313 nm corresponding to the doped crystals.

In order to understand the energy transfer mechanism from  $Gd^{3+}$  ions to  $Ce^{3+}$  ions, the temperature dependence of the emission band at 400 nm corresponding to the excitation at 312 nm and 345 nm has been measured and is shown in Fig. 3.10 (a) and Fig. 3.10 (b) respectively. The emission band gets resolved into two separate peaks at 386 nm and 414 nm. The origin of these two peaks lies in the spin orbit splitting of the ground level of  $Ce^{3+}$  into  ${}^{2}F_{5/2}$  and  ${}^{2}F_{7/2}$  energy levels [145]. The temperature dependence of the integrated intensity from the 400 nm emission has been plotted for the excitation at 312 and 345 nm and is shown in Fig. 3.10 (c). The temperature dependence response from the same  $Ce^{3+}$  centers were found to be different

when excited at the two excitation bands of 312 and 345 nm respectively and can be understood in terms of the energy transfer from the  $Gd^{3+}$  centers to  $Ce^{3+}$  centers [146]. Thermal quenching has been observed for the emission at 400 nm when excited at 345 nm whereas the intensity of the same emission at 400 nm for an excitation of 312 nm remains almost constant in the temperature range from 77K to 300K. The inverse thermal quenching of  $Gd^{3+}$  compensates for the thermal quenching taking place in  $Ce^{3+}$  centers. Furthermore this energy transfer was expected to affect the decay kinetics of the LGBO:Ce single crystals. It was found that when the LGBO:Ce is excited at  $Ce^{3+}$  centers, it shows a fast single exponential decay which is characteristic of the  $Ce^{3+}$ emission whereas the excitation corresponding to 312 nm for the same emission band shows a much slower decay kinetics with a decay time in the range of few microseconds[147]. The decay kinetics of the emission from the  $Gd^{3+}$  and the  $Ce^{3+}$  centers at 313 nm and 400 nm respectively have been compared for the doped and the undoped single crystals and has been plotted and shown in Fig. 3.12 and Fig. 3.13 respectively.



Figure 3.10 (a): Temperature map of the Ce<sup>3+</sup> emission at 400 nm for excitation at 312 nm.

Figure 3.10 (b): Temperature map of the  $Ce^{3+}$  emission at 400 nm for excitation at 345 nm.



Figure 3.10 (c): Temperature dependence of absolute intensity of emission at 400 nm for the two excitations ( $\bigcirc$ -312 nm and  $\square$ -345 nm).



Figure 3.11: Decay kinetics of the emission at 400 nm at an excitation at 312 nm). Red line shown exponential fit.

It became evident from the measurement that when the cerium is excited completely in a indirect way (at 274 nm, excitation of  $Gd^{3+}$ ), the longer life time component gets increased in comparison to the excitation at 312 nm where both direct and indirect excitation takes place. The decay constant has been found to be increased with temperature as seen from the temperature dependence of the decay kinetics at 400 nm corresponding to an excitation of 274 nm. An involvement of a barrier in the energy transfer mechanism similar to that seen in the intensity profile of the emission at 313 nm from  $Gd^{3+}$  centers in case of cerium doped single crystals has been observed above 200K which is characterized by a sudden increase in the fast decay component (~ 300 µs). All these above observations indicate that the emission at 400 nm in the LGBO:Ce is contributed through two different routes leading to two different temperature dependences and decay profiles. The contributions from Gd centers are so predominant that it could not be completely eliminated.



Figure 3.12: Decay profile of emission at 313 nm for excitation at 274 nm.



Figure 3.13: Decay profile of emission at 400 nm for excitation at 274 and 312 nm.

#### **3.3 Conclusion**

Good quality undoped and cerium doped LGBO single crystals were grown using Czochralski technique. Grown single crystals were crack free and did not contain any visible defects. They showed overall a transparency of nearly 80 % in the range of 300 nm to 1100 nm. The low temperature photoluminescence studies showed two different temperature dependence for the Ce<sup>3+</sup> emission at 400 nm when excited at 345 nm (directly into the Ce<sup>3+</sup> band only) and at 312 nm (into Ce<sup>3+</sup> band as well as energy transfer from at Gd<sup>3+</sup> centers). The intensity of emission band at 400 nm remains constant in the 77-300 K temperature range for the excitation at 312 nm, due to energy transfer from Gd<sup>+3</sup> ions to Ce<sup>3+</sup> ions while at 345 nm excitation it quenched with temperature. A kind of activation energy was also found to be operating in the energy transfer mechanism between Gd and Ce centers. The decay kinetics of the emission at 400 nm showed the presence of a long life time component due to energy transfer mechanism which may be a drawback for the material as a scintillator as it will difficult to distinguish between two events in a high flux environment. Further, since the material is proposed to be used a thermal neutron scintillator and the interaction of thermal neutrons with gadolinium results in a gamma shower of energy in the range of 1 to 8 MeV approximately, it will be difficult for the

scintillator to capture this high gamma energy due to low density of the material. Due to this the Compton background is expected to be high which will make it difficult to resolve the photo peak due to thermal neutrons in the pulse height spectrum. A possible remedy for this could be the replacement of the gadolinium with other possible trivalent elements like Lutetium (Lu) and Yttrium (Y) which are not expected to affect the luminescence properties of the material in such detrimental way.

## **CHAPTER 4**

# <u>Growth and Characterization of Li<sub>6</sub>Lu(BO<sub>3</sub>)<sub>3</sub></u>

## **4.1 Introduction to material**

The single crystals of Lithium lutetium borate (LLBO) are another promising member of the borate group family which can be used as a thermal neutron detector. The presence of <sup>6</sup>Li (natural abundance 7.4%,  $\sigma_{abs} = 940$  barns) and  $^{10}B$  (natural abundance 20%,  $\sigma_{abs} = 3835$  barns) even in their natural isotopic ratio can offer significant efficiency for the thermal neutrons because of the presence of their number in the unit cell [117, 120, 147]. The LLBO:Ce matrix efficiently transfers the energy deposited by the charged particles produced during the interaction of thermal neutrons to the luminescent Ce<sup>3+</sup> centers present in this material. This results in a blue emission band at ~ 390 nm arising from the 5d to 4f transitions in  $Ce^{3+}$  centres similar to that observed in the LGBO:Ce matrix [149]. However, the emission from the gadolinium centers was not present and lutetium doesn't have its emission in the visible region. Hence, the luminescent properties of this material are solely governed by the Ce<sup>3+</sup> centers. It makes these scintillators faster in comparison with LGBO:Ce where the energy transfer from the Gd<sup>3+</sup> to Ce<sup>3+</sup> centres dictates the decay mechanism. Cerium doped Li<sub>6</sub>Lu(BO<sub>3</sub>)<sub>3</sub>: LLBO exhibits a combination of fast decay (30ns) and a moderate light output that can be easily read out using the standard scintillator electronics [150]. This was one of the main reasons behind choosing this material for the single crystal growth by tackling some of the problems associated with the LGBO single crystal scintillators. However, a larger difference in the ionic radii between the cerium and the lutetium was expected to create some problems during the crystal growth. The presence of radioactive isotopes of lutetium in a decent ratio in the naturally available form also leads to an inherent background in the material [151]. However, initial studies performed over polycrystalline samples and literature survey suggested that a higher cerium concentration can be incorporated in the LLBO matrix which could be an advantage as it will improve the luminescence properties and consequently the scintillation characteristics of the material. Thermal quenching was also not reported in this material in the polycrystalline form which makes it a promising candidate to be grown and characterize in the single crystal form. Though the borates are flagged with some common growth characteristics, still we found a large variation in the thermal properties and the reaction kinetics observed during the single phase formation. The fast decay kinetics already reported from the Ce<sup>3+</sup> centers is certainly an advantage while investigating this material as a thermal neutron detector as the dead time will be small and a better counting efficiency could be achieved [152]. All these properties associated with material motivated the work carried out and presented in this chapter.

#### 4.2 Experimental Procedure

Single crystals of 0.2 % Ce doped LLBO were grown from their melts using the Czochralski technique (Cyberstar make Oxypuller). The single phase starting charge has been prepared by mixing high purity (99.99%) constituents oxides (Li<sub>2</sub>CO<sub>3</sub>, Lu<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, H<sub>3</sub>BO<sub>3</sub>). The materials were mixed thoroughly and sintered at 350°C first to remove the moisture and other gases produced during the decomposition of the boric acid (H<sub>3</sub>BO<sub>3</sub>) in the presence of other constituent oxides. This ensures that when the further synthesis procedure of the starting charge will be carried out using the pre-sintered charge at 350°C, the phase uniformity of the material shall be maintained after the reaction which is otherwise becomes a hard lump and interferences with the phase formation during sintering. The as-prepared material was loaded in a platinum crucible and heated to its melting point (850°C) using an RF generator. The growth station for the growth of LLBO has been modified to achieve a higher axial thermal gradient by removing any active or passive after heater above the crucible. A high thermal

gradient of ~  $100^{\circ}$ C/cm just above the melt could be therefore achieved in these growth experiments. The pull rate for the crystal growth initially during the seed region was kept to be 0.2 mm/h which was further increased to 0.5 mm/h during the cylindrical region of the growth. The rotation of the growing crystal was fixed at 10 rpm during the entire crystal growth. A baxis (010) oriented seed have been used for the growth of single crystals. The grown crystals were cooled down to the room temperature at a rate of 30°C/h. Powder XRD (Rigaku make RINT-2200) and DTA (SETRAM make DTA-TG 92) measurements were performed to analyse the phase of the material. The X-ray intensities for the diffraction peaks were recorded in the range of  $10-80^{\circ}$  (20) with a step of  $0.02^{\circ}$  and a scan speed of  $1^{\circ}/\text{min}$ . For the DTA, the samples were heated at a rate of 10K/min and kept at the melting point for 300 seconds before cooling down the melt again at a rate of 10K/min down to the room temperature. The Radioluminescence characteristics have been recorded with the white Cu tube X-ray excitation at an accelerating voltage of 40kV and 30 mA of tube current and measuring the emission by employing a monochromator and PMT (make: PI Acton spectra pro SP-2300). Photoluminescence studies were performed over a wavelength range from 250 - 800 nm at room temperature employing a fluorescence spectrometer (Edinburg Model-FLP920). The emission was recorded in the reflection geometry mode by positioning the sample at 45° with respect to the excitation beam. A spectral bandwidth of 1 nm was selected for both excitation and emission arms while recording the emission characteristics from the sample under the exposure from a steady state xenon lamp. The recorded luminescence spectra were corrected for the spectral sensitivity with the instrument response function. A nitrogen gas filled flash lamp operating at a repetition rate of 40 kHz was employed for recording the life-time characteristics of the photoluminescence decay. The samples have been excited at a wavelength of 360 nm using nitrogen emission lines and the temporal response of the luminescence at 410 nm was recorded. The instrument response function was also recorded by keeping a reflector in place of the sample.

## 4.3 Results and discussion

Fig.4.1 shows the result of various crystal growth attempts carried out in the process to optimize the parameters. The initial crystal growth attempts leads to a foggy appearance of the single crystals due to the high viscosity of the melt which makes it difficult to thermalise once the melting of the material has been achieved. Hence, it takes longer duration to homogenize the melt after reaching the melting temperature [126].



Figure 4.1: Photographs of as-grown single crystal of Li<sub>6</sub>Lu(BO<sub>3</sub>)<sub>3</sub>.

In our case, the melt was kept for nearly four hours at the melting temperature so that the uniformity in the melt could be achieved. Usually, bubbles are found within the melt surface and the homogenization of the melt minimizes the bubbles present over melt surface with time. The bubbles could not be completely removed even after long hours of melt homogenization and it makes it challenging to initiate the nucleation by bringing the seed crystal in contact with the melt. Hence, the initial pull rates of the single crystals were brought down to 0.25 mm/h and a comparatively higher rotation rate of  $\sim 15$  rpm was used to expel the bubbles from the solid melt interface where the nucleation takes place. This is well reported feature in the growth of

borates (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) with similar thermal properties where a high thermal gradient along with a slow pull rate has been employed to achieve highly transparent and bubble free single crystals [153]. Apart from this the initial nucleation of the single crystals was carried out at temperature slightly above the melting point at which the melting rate of the seed crystal is slow and it allows to nucleate a thermally stable single grain. The nucleation initiated at approximately 50°C higher temperature than the melt temperature, results into the growth of a transparent crystal ingot which could be seen in crystals photographs showing a gradual increase in the quality of the as grown single crystals from left to right. Though the most challenging part was the cracking of these single crystals due to the presence of the cleavage planes present in this group of borates. Single crystal growth attempts have been tried along the "b-axis" oriented seed along which the crack free single crystals of LGBO has been pulled as described in the previous chapter. Passive after heater has also been used to minimize the thermal gradient and the crystals were annealed near melt temperature after the completion of the crystal growth. But none of these have been able to completely solve the cracking problem associated with the LLBO:Ce single crystals. A low temperature gradient leads to the growth in a polycrystalline phase whereas crystal growth under high temperature gradient could yield transparent crystals but develops cracks either during growth or cooling. The melting and the freezing behaviour of LLBO:Ce have been shown in Fig. 4.2.



Figure 4.2: Melting and freezing behaviour of the Li<sub>6</sub>Lu(BO<sub>3</sub>)<sub>3</sub>.

It clearly shows a single endotherm at 830°C corresponding to the melting of the LLBO:Ce. However, during the cooling sequence it showed two sharp exotherms in the temperature region of 600°C to 700°C. The DTA plot of both the starting charge and the grown crystals resembles the same and even the repeated heating of the melt could not remove the two peaks present in the freezing pattern of the LLBO:Ce. This suggest some inherent property of the material which was also observed in transparent chunks of the as grown single crystals which could otherwise should have shown a different behaviour after reheating. Even during the second melting where two peaks have been observed, shows a single exothermic peak, corresponding to sharp melting which is a characteristic feature of the single phase of the material. The presence of other phase of the materials should have showed the signature of its presence. Whereas once again in the freezing profile, it showed multiple peaks which has been reported commonly in these family  $(Li_6Re(BO_3)_3)$  of borate crystals which occurs due to crystallization at several temperatures [154, 154]. The powder XRD pattern has been shown in Fig. 4.3. The XRD measurements revealed monoclinic structure with the lattice parameters closely matching with the reported values.



Figure 4.3: Powder XRD pattern of Li<sub>6</sub>Lu(BO<sub>3</sub>)<sub>3</sub>.

All the peaks corresponding to the Braggs reflection could be matched with the ICDD phase of the  $Li_6Y(BO_3)_3$  and other literature values. The absence of any extra peaks suggests the absence of any foreign phases within the XRD limit of the detection. The excitation and the emission spectrum from the LLBO:Ce has been shown in Fig. 4.4.



Figure 4.4: Excitation and emission spectrum of 0.5 % Ce doped LLBO

The emission spectrum for the single crystals showed a broad emission peak peaking at ~ 400 nm which consists of two peaks visibly seen at room temperature. This broad emission band corresponds to the 5d $\rightarrow$ 4f transition from Ce<sup>3+</sup> [155]. The two peaks arise due to the splitting of ground 4f level of Ce<sup>3+</sup> into <sup>2</sup>F<sub>5/2</sub> and <sup>2</sup>F<sub>7/2</sub> due to spin-orbit coupling [156]. However, these could not be resolved at room temperature in the iso-structural LGBO:Ce single crystals. This splitting indicates a different crystal field environment around the Ce<sup>3+</sup> centers. It could also be seen that there is an overlap between the excitation band at 350 nm and the emission band at 400 nm. This narrow stokes's shift is expected to get shorter with increasing the concentration of cerium and hence a concentration quenching is suggested at relatively lower concentration. To understand this radio-luminescence spectrum has been recorded on pellet samples for various concentrations of cerium in the LLBO matrix. The normalised spectrum of the radio-luminescence has been shown in Fig. 4.5. It clearly shows no shift in the position of the emission band with increasing cerium concentration. Even the absolute intensity barely changes at higher concentration at a given fixed orientation and position of the sample from the excitation source.



Figure 4.5: Radio-luminescence spectra from LLBO:Ce having various cerium concentration

The decay profile for the LLBO:Ce shows the signature characteristics of the  $Ce^{3+}$  centers and shows a single exponential decay with a decay time of ~ 30 ns and is shown in Fig. 4.6. The instrument response function has already been corrected before fitting the exponential decay.



Figure 5.6: Decay profile of the LLBO:Ce

## 4.3 Conclusion

Good quality 0.2% cerium doped LLBO single crystals were grown using the Czochralski technique. The single crystals were found to be cracked due to stress generated from the growth under high temperature gradient and presence of the cleavage plane. The transparent portions of the grown crystals were free from any visible defects and bubbles. The PL spectrum shows emission band peaking at 400 nm arising from  $Ce^{3+}$  centers with excitation bands at 350 nm. The LLBO:Ce exhibited a fast decay kinetics with a single exponential fit and the time constant was in the range of 25-30 ns. This fast decay is a desirable property of the scintillator which is an advantage over the LGBO:Ce single crystals which were flagged with a slow decay due to

the presence of the gadolinium atoms in the material. The interaction of thermal neutrons is also much simpler in this material due to generation of only charged particles when the thermal neutrons interacts with the LLBO:Ce matrix unlike in LGBO:Ce where it also results in a gamma shower due to thermal neutron capture by Gd.

# **CHAPTER5**

# **<u>Growth and Characterization of Li<sub>6</sub>Y(BO<sub>3</sub>)</u>**

## 5.1 Introduction to material

Among the cerium doped lithium rare earth borates likeLi<sub>6</sub>Gd(BO<sub>3</sub>)<sub>3</sub> (LGBO), Li<sub>6</sub>Lu(BO<sub>3</sub>)<sub>3</sub> (LLuBO) and Li<sub>6</sub>Y(BO<sub>3</sub>)<sub>3</sub> (LYBO), the application of LGBO in a mixed background of neutrons and gamma radiation gets difficult due to the generation of continuum gamma after capturing thermal neutron by Gd. Another major problem with LGBO is its slow decay time of  $\sim 250 \ \mu s$  due to the energy transfer from Gd<sup>3+</sup> to Ce<sup>3+</sup> centers [141]. The replacement of gadolinium ions by yttrium ions is expected to have the faster response and it will also decreases the effective atomic number to reduce the gamma sensitivity [157]. There is no energy level band arising due to  $Y^{3+}$  centers near the 420 emission due to  $Ce^{3+}$  ions which otherwise would have affected the emission characteristics from this sample. The cerium replaces the rare-earth ion (Yttrium in this case) in these borate crystals and therefore it is required for them to remain in the trivalent state which is lesser stable and easily oxidized to the Ce<sup>4+</sup> state if the growth is carried out in an oxidizing environment. The Ce<sup>4+</sup> is nonradiative in nature and its presence with  $Ce^{3+}$  affects the light output from the material [128]. Therefore the growth ambient for these single crystals is very important parameter as they will strongly affect the luminescence properties. The single crystal growth of these borates is already known to be difficult and the effect of ambience is going to add another parameter for investigation as the formation of metastable phases may have a role which can be caused by the ambient [154,158]. The presence of cleavage plane adds to the already existing list of problems present in this family of borates [159]. As far as the literature for the growth of cerium doped LYBO is concerned, it is limited and contains little information about the growth behaviour of

this material. Most of the available literature is available on the measurements performed over polycrystalline samples. Hence it is quite necessary to investigate this material in detail because of its promising features among the other member of the family. LYBO:Ce has the combination of a matching emission with Bialkali PMT and a fast decay to make it a suitable candidate to grow it in the single crystal from. It has a reasonable light-output of about 1200ph/MeV which is decent enough to be collected by the standard pulse processing chain [160, 161].

#### 5.2 Experimental Procedure

The single crystals of Ce doped Li<sub>6</sub>Y(BO<sub>3</sub>)<sub>3</sub> [LYBO] were grown from their melts using the Czochralski technique. The starting charge for the growth has been prepared from the 4N pure (99.99%) constituents oxides (Li<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>) using the high temperature solid state reaction. For this the initial mixture which was thoroughly mixed was heated at 350°C to ensure decomposition of the boric acid and removal by products. The mixture was then crushed and mixed thoroughly again to heat it at 700°C again. This procedure is repeated twice to achieve a homogenize mixture of the desired phase. As prepared material was taken in form of pellets in a platinum crucible and heated up to 50°C higher temperature than its melting point [865<sup>o</sup>C] to homogenize the melt. The single crystal pulling was carried out using an LBO  $(Li_2B_4O_7)$  seed crystal as it contains the same constituent elements, though it has a different crystal structure. Since the melting temperature of the LGBO and LLBO were lower than the LYBO and their seed could not have been used as during melting of the seed, undesired impurity phases could have been mixed with the LYBO phase.Powder XRD (Rigaku make RINT-2200) of the starting charge and the grown crystal from their various regions were taken to determine the phase uniformity of the material. The measurements were performed at a scan speed of  $1^{0}$ /min with a step size of  $0.02^{0}$  over a 2 $\theta$  ranging from  $10^{0}$  to  $80^{0}$  for the polycrystalline powder. Differential Thermal Analyser (SETRAM make DTA-TG 92) were

performed on the starting charge and the samples from grown crystals to verify the single phase formation by heating and cooling the sample at a scan speed of 10K/mins and the heating and cooling profile were corrected for the blank response for the TG-DTA. The TG response has been carefully studied to see the evaporative losses during the heating and the cooling sequence. Finally, as grown single crystals were cut and processed for optical and electronic characterization. Samples for optical measurements were polished down to the mirror finish using alumina powders down to 0.3 µm size. A UV-Vis spectrophotometer Shimadzu (UV-3600) has been used to record the transmission spectra in the wavelength range from 200 nm to 1100 nm. PL studies were performed over a wavelength range from 200 nm to 800 nm at room temperature employing a fluorescence spectrometer (Edinburg Model-FLP920). For low temperature studies a cryostat (Oxford, Optistat-DN) was used which was controlling the temperature in a closed loop using Peltiercooling. A reflection geometry mode was used where the sample is positioned at 45° with respect to the excitation beam and the recorded spectrum was corrected for the instrument response function. The excitation spectrum has been recorded by mixing the monochromator at the emission arm at fixed wavelength and scanning the monochromator at the excitation arm. Finally, the excitation spectrum was corrected by dividing the intensity of the excitation spectrum by the lamp's spectrum to correct spectrum anomaly arising from the relative intensity difference in the excitation spectrum. A steady state xenon lamp was used as an excitation source and a spectral bandwidth of 1 nm was selected for both excitation and emission arms. A flash lamp consisting of nitrogen gas operating at a repetition rate of 40 kHz was employed for recording the life-time characteristics of the photoluminescence decay. The nitrogen emission lines at 360 nm were used to excite the samples and the temporal response of the luminescence from the LYBO:Ce was recorded. Finally, the instrument response function was also recorded by keeping a reflector in place of the sample and a correction was made using this for the measurements performed.

## 5.3 Results and discussion

Fig. 5.1 shows the photographs of the as grown single crystals of LYBO:Ce. The photographs have been presented in such a way that the pictures from left to right represents the optimisation of the growth parameters to achieve the transparent and crack-free single crystal of LYBO:Ce. The single crystals, grown under low temperature gradient, result in to a milky polycrystalline ingot. This may be assigned to the inability for achieving a thermodynamically stable nucleation causing a large number of nuclei present at the solid melt interface which does not migrate in the low temperature gradient and solidifies in to a polycrystalline ingot. However, a controlled nucleation at a temperature approximately 50 °C higher than the melt temperature using an LBO seed results into a transparent ingot grown as a polycrystalline aggregate [162]. This could be further improved by employing higher temperature gradient of approximately 100°C/cm just above the melt by removing any form of after heater (passive insulation) above the crucible.



Figure 5.1: Photographs of as-grown single crystal of Li<sub>6</sub>Y(BO<sub>3</sub>)<sub>3</sub>.

The single crystals grown under high temperature gradient with a pull rate of less than 0.5 mm/h result into a transparent and crack-free single crystal ingot.


Figure 5.2: Melting and freezing behaviour of the Li<sub>6</sub>Y(BO<sub>3</sub>)<sub>3</sub>.

The results of the melting and the freezing behaviour studied using TG-DTA has been shown in Fig.5.2. It shows a broad single peak for the melting while the freezing is characterized by a very narrow freezing profile (width of  $\sim 1.5$  K) and a very large magnitude of super-cooling ( $\sim 200$  K) [147,163]. Although the large super cooling observed here is a common feature for this borate family but the magnitude of super-cooling observed in LYBO ( $\sim 250$ K) is much larger than the ones exhibited by LGBO and LLBO ( $\sim 100-150$ K). This was one of the major reasons for the milky growth of the LYBO under low temperature gradient and relatively higher pulls rates which were reported by other authors as well [164]. The Powder XRD pattern of the grown single crystal is shown in Fig.5.3. The phase of the material has been verified by matching the Bragg's reflection from those listed in the standard JCPDS data. The lattice parameters are calculated that matches well with the reported crystal structure data.



Figure 5.3: Powder XRD pattern of Li<sub>6</sub>Gd(BO<sub>3</sub>)<sub>3</sub>.

The transmission spectra for the 0.2 % Ce doped LYBO has been shown in Fig. 5.4. It shows a transmission of more than 80% in the wavelength range of 300 nm to 1100 nm. No absorption bands have been found in the transmission range of the LYBO:Ce single crystals.



Figure 5.4: Transmission spectra of 0.1% Ce doped single crystals of Li<sub>6</sub>Y(BO<sub>3</sub>)<sub>3</sub>

However, a broad absorption band at 350 nm was observed due to the charge transfer from Ce<sup>4+</sup> to O<sup>2-</sup>in the LYBO:Ce matrix [162, 165, 166]. The excitation and the emission spectra of 0.1 % cerium doped LYBO is shown in Fig.5.5. It shows a broad emission band, peaking at ~ 420 nm which corresponds to the transition of electron in the Ce<sup>3+</sup> from 5d→4f energy levels [157].



Figure 5.5: Excitation (black dotted line) and emission (red solid line) spectra of Li<sub>6</sub>Y(BO<sub>3</sub>)<sub>3</sub>:Ce crystal.

This could be de-convolute into two peaks originating from the splitting of  $Ce^{3+}$  ground level into  ${}^{2}F_{5/2}$  and  ${}^{2}F_{7/2}$  due to the spin orbit coupling [145]. Two excitation bands peaking at 350 nm and at 310 nm could be found corresponding to emission at 420 nm as shown in the inset of Fig.5.5. The emission characteristics of the LYBO:Ce strongly depends upon the ambient in which the growth is carried out as the reducing ambient favour the  $Ce^{3+}$  ions going in to the matrix while the growth in a oxidising environment (air or partial oxygen) leads to the  $Ce^{4+}$ states being favoured [128]. This gives rise to oxygen related defects due to charge imbalance and the emission characteristics got affected detrimentally. To understand the role of ambience during the single crystal growth on the luminescence characteristics of the LYBO:Ce, the low temperature studies have been carried out. The temperature dependence of the emission at 410 nm for the samples grown in air ambient has been shown in Fig. 5.6. The inset of the graph shows the comparison of the excitation at 300 and 77 K, corresponding to the emission at 420 nm. The emission band centered around 400 nm shows very small variation in the intensity with temperature.





The temperature dependence of the emission at 410 nm shows different behaviour in case of samples grown in argon ambient and is shown in Fig. 5.7. The inset of the graph shows the comparison of the excitation bands at 77 K and 300 K. The integrated intensity of the emission band at 410 nm for the samples grown in air and argon has been shown in Fig. 5.8. It has been found that the intensity of the emission band at 410 nm decreases with temperature for the

samples grown in argon. The difference in the behaviour of the temperature dependence of the emission can be understood in terms of the fact that the growth in argon ambient minimises the presence of Ce<sup>4+</sup> ions in the LYBO matrix which are non-radiative but creates oxygen related defects which competes as alternative centers of absorption of this luminescent energy. The increase in temperature enhances this effect. Hence, the crystal growth carried out in oxygen ambient doesn't show this behaviour due to absence of oxygen related defects.



Figure 5.7: Temperature map of the emission at 410 nm due to Ce<sup>3+</sup> centers for the samples grown in argon

This enhanced excitation band at 300 K helped the emission intensity from getting thermally quenched in air grown samples as compared to Argon grown samples. The reason for this thermal quenching could be defects related to the oxygen vacancies which can be found in air grown samples. Since the Ce<sup>4+</sup> is the stable oxidation state of cerium, and the cerium in LYBO replaces a trivalent ion it creates certain defects to create the charge balance in the lattice. When the single crystals are grown in air ambient, those defects get compensated. On the other hand, the growth in argon ambient further creates oxygen related defect centers which start

quenching the luminescence intensity. The Photoluminescence decay measured for the 410 nm emission from the  $Ce^{3+}$  centers have been recorded and is shown in Fig. 5.9.



Figure 5.8: Comparison of the integrated intensity of the temperature dependence of the emission at 410 nm due to  $Ce^{3+}$  centers for the samples grown in (a) Air (b) Argon



Figure 5.9: Photoluminescence decay of the emission from the Ce<sup>3+</sup> centers at an excitation of 330 nm approx.

The spectrum fits into a single exponential decay with an average life time of  $\sim 25$  ns which is characteristic of the Ce<sup>3+</sup> emission [157]. Fast decay is a desirable property for detector applications and thus makes this material suitable.



Figure 5.10: Radio-luminescence decay from LYBO:Ce for thermal neutrons and gamma rays

The scintillation decay of the LYBO:Ce has been measured to understand the decay mechanism of the  $Ce^{3+}$  emission resulting from the excitation from gamma rays and the neutrons. It shows difference in decay times due to gamma and neutrons which mainly arises due to the way the excitation is caused by the two radiations [157]. While on one hand the interaction of neutron created charged particles which get absorbed in a short range, the excitation through gamma radiation results in a relatively slow decay.

#### 5.4 Conclusion

Single crystals of 0.1% Ce doped  $Li_6Y(BO_3)_3$  were grown from their melts using the Czochralski technique. The optimized parameters for the growth of LYBO:Ce single crystals

were grown at a pull rate of 0.5 mm/h and along with the rotation rate of 10 rpm during the entire growth duration. The grown crystals were crack-free crystals and free from any visible defects. The transmission spectra showed more than 80% transmission and the crystal were transparent to its own emission. The PL spectrum shows an excitation at 310 and 350 nm and emission at 420 nm which is typical of Ce<sup>3+</sup>. A decay time of 25 ns has been obtained that makes this material highly suitablefor radiation detector applications. The scintillation decay profile showed difference in the decay constants for the gamma and neutrons. This difference though small may be significant with respect to the pulse shape discrimination required to separate the pulses arising from the neutrons and the gamma rays. This could be significantly important as far as the use of scintillator is concerned in the mixed fixed background of gamma and neutrons in areas like neutron detector.

## **CHAPTER6**

# **Chapter 6 (Fabrication of Neutron Detector and**

## <u>measurements)</u>

#### **6.1 Introduction to thermal neutron detection**

Lithium rare earth borates (Li<sub>6</sub>R(BO<sub>3</sub>)<sub>3</sub>; R= Gd, Lu & Y) have a combination of nuclei which have a large cross-section for thermal neutrons. The nuclear reaction of the thermal neutrons with the <sup>6</sup>Li (natural abundance: 7.4%;  $\sigma_{abs}$ : 940 barns), <sup>157</sup>Gd (natural abundance: 15%;  $\sigma_{abs}$ : 255,000 barns) and <sup>10</sup>B (natural abundance: 20%;  $\sigma_{abs}$ : 3835 barns) produce charged particles and gamma radiation which deposit their energy in the scintillator [168]. The optical and electronic properties of these materials allow doping of suitable rare-earth ions due to their large band gap to capture this energy for detecting the events [141]. The lithium rare-earth borates, activated with Ce<sup>3+</sup> ions have a fast and efficient visible emission in the blue region at about 400 nm [141]. The efficiency response of a bi-alkali photomultiplier tubes (PMT) matches well with this emission and therefore can be easily employed as a read-out device using standard electronics. These borates have reasonable light output in the range of 1000ph/MeV to 10000ph/MeV which can be processed in electronic form to count the thermal neutron interaction events [139,169]. The thermal, structural, optical and electronic properties of these materials have already been discussed in the earlier chapters on the basis of which it has been concluded that high efficiency thermal neutron detectors can be fabricated using the processed scintillators from these materials. This chapter deals with the fabrication of solid state neutron detectors based on the scintillators processed from as-grown single crystal of lithium rare-earth borates. The fabricated detectors have been used to detect thermal neutrons generated from different sources having fluxes ranging from  $10n/cm^2/s$  to  $10^7n/cm^2/s$ .

### **6.2 Experiments**

The cerium doped (0.2 mole%) single crystals of LGBO, LLBO and LYBO were grown using the Czochralski technique in an automatic diameter controlled crystal puller system (Model: Oxypuller, Cyberstar) as described in earlier chapters. Scintillators were processed in circular cross-sections from as-grown single crystals by cutting ingots using an SS wire saw of 0.5 mm diameter under continuous slurry of silicon carbide. The scintillators were then polished with alumina powder down to thickness of 0.3 micron on one face to finally achieve scintillators of 20 mm diameter and 2 mm thick to optically couple with photo-sensors like PMT. For optical coupling with SiPM, the scintillators have been processed in 6x6 mm<sup>2</sup> size. The polished face of the scintillator crystal was optically coupled to a photo-multiplier tube (2 inch PMT, Hamamatsu Model No. R2154) using a silicon gel from Dow Corning. The silicone gel acts as a refractive index matching fluid and minimizes the losses arising due to the poor optical contact between the scintillator and the PMT and the losses from the total internal reflection. The scintillator crystal was then wrapped with 8-10 layers of reflecting Teflon tapes (thickness  $\sim 0.1$  mm) and has been finally wrapped with an aluminum foil. The reflecting tapes ensure efficient collection of light towards PMT while Al foil helps minimize the dark-current of the PMT. The anode signal from the PMT is connected to a pulse processing chain consisting of a pre-amplifier, a shaping amplifier and an 8k MCA to measure pulse-height spectra. Compact devices have been fabricated by mounting the scintillator over PMT and encapsulating the assembly in a cylindrical SS housing. The entire electronics (commercial) for the pulse processing chain was mounted on the back of the PMT on electronic circuit board. The entire assembly has been powered using a 5V supply form the USB and a DC-DC converter has been

used to power the PMT as well. The stability of the voltage for powering PMT has been checked for longer durations before performing the measurements. The laboratory gamma sources (<sup>137</sup>Cs, <sup>60</sup>Co) having activities in the range of micro-Curie were used to characterize the scintillators. Charged particle detection has been carried out using an Am-Pu source with alpha energies of 5.2 MeV and 5.5 MeV. The scintillators have been coupled directly to the alpha source by collimating the alpha beam and the entire assembly has been wrapped with Teflon tape for efficient collection of light. The alpha source has been collimated by wrapping the source in an aluminum foil and making a small aperture in the coupling face of the source with the detector. The pulse height spectrum has been recorded by connecting the signal from the anode of the PMT to the pulse processing chain. For detection of thermal neutrons a photon counting setup (Hamamatsu C9744) was also used for the measurements in counting mode. For this the detector counts were recorded using the photon counting unit under the exposure of the detector under neutron beam from a nuclear reactor. Later the neutron beam has been closed by putting a cadmium sheet and the response of the gamma background was recorded to compare the counts due to neutron and the gamma interaction of the detector. The pulse-height spectra (PHS) were also recorded for the thermal neutrons from the Dhruva nuclear reactor with a flux of about 10<sup>7</sup>n/s/cm<sup>2</sup>. Radiation shields like lead brick (for gamma-rays) and borated rubber (for neutrons) were used to discriminate spectra originating from neutron and gamma-rays, respectively. The pulse-height spectra have also been recorded for other neutron sources such as <sup>252</sup>Cf and Am-Be that have different fluxes under same gain setting to compare the response of the detectors to the thermal neutrons. The scintillation decay of the crystals were determined by recording the anode pulse of the PMT using a fast digital oscilloscope (Tektronix, MDO -3102) having 1 GHz bandwidth. The decay time was measured for both neutrons and gamma exposures.

### 6.3 Results and discussion

Fig. 6.1 shows the photographs of the as-grown single crystals of  $Li_6Gd(BO_3)_3$  (LGBO),  $Li_6Lu(BO_3)_3$  (LLBO) &  $Li_6Y(BO_3)_3$ (LYBO) (left to right). The photograph on the extreme right shows the as-grown single crystal of LYBO under UV light which clearly shows the scintillation emission from these crystals. The emission from this family of borates (LGBO, LLBO & LYBO) lies in the blue region (near 400 nm approx) which matches well with the efficiency response of the Bialkali PMT which is the most common photo sensors.



Figure 6.1: (a) Single crystals of Li<sub>6</sub>R(BO<sub>3</sub>)<sub>3</sub>:Ce [LGBO, LLBO & LYBO (L to R)]

#### (b) Single crystal of LYBO under UV

A compact detector fabricated from the scintillators coupled to the PMT is shown in Fig. 6.2. It shows the entire pulse processing chain within a cylindrical housing containing the PMT which has been powered through a USB of a laptop. This makes the device portable in true sense as heavy NIM bins are not needed and the field measurements can be carried out beyond the laboratory.



Figure 6.2: Compact detector fabricated using LYBO couple with PMT

For laboratory measurements the NIM bin based nuclear modules were used to record the pulse-height spectrum using the developed scintillation detector.

#### 6.3.1 Scintillation characteristics of LGBO

The excitation and emission of the LGBO:Ce characteristics were already explained in the earlier chapters which showed matching characteristics with the PMT for detector fabrication. The pulse-height spectrum recorded for the <sup>137</sup>Cs and <sup>60</sup>Co gamma energies has been shown in Fig. 6.3 (a) and Fig. 6.3 (b) respectively. It shows an unresolved photo-peak at a channel number of ~ 130 corresponding to the energy of 662 keV from the <sup>137</sup>Cs source. The pulse-height spectrum has been observed at a low channel number and the contribution from mainly Compton is present due to the effective atomic number of the scintillator. A very thin disc of the detector has been used for the measurements to impart low sensitivity to gamma radiation compared to thermal neutron. The PHS due to Co<sup>60</sup> shows the photo-peak at ~ 250 channel

number which remains unresolved due to the reasons stated earlier. The low channel number has relatively large backgrounds from the electronic noise. The pulse-height spectrum due to alpha particles from an Am-Pu source has been recorded and shown in Fig. 6.4 (a). It shows a single



Figure 6.3: (a) Pulse height spectrum due toFigure 6.3: (b) Pulse height spectrum due toCs-137 recoded using LGBOCo-60recoded using LGBO

broad photo-peak at a channel number of ~ 100 due to the alpha energies of 5.2 MeV and 5.5 MeV. The detector could not resolve the two peaks due to a poor energy resolution mainly due to its low light output [123,157, 171]. Though the detection of alpha particles confirms the capability of the detector to detect thermal neutrons which will eventually produce charged particle within the detector as a result of the (n, $\alpha$ ) reaction. One more reason for the poor resolution of the alpha energies could be the attenuation of the alphas energies before reaching the detector as the experiment has been carried out by placing the alpha source in contact with the detector and no vacuum was used during the experiment. The detector has been further employed to measure the pulse-height spectrum due to thermal neutrons. The pulse-height spectrum recorded for thermal neutrons suing LGBO detector is shown in Fig. 6.4 (b). A <sup>252</sup>Cf source was used from which the fast neutron were thermalised using polythene blocks. It shows

signatures of two peaks at a channel number of 200 and 375 which correspond to the interaction of thermal neutrons with the scintillator and the Q value deposited due to the nuclear reaction. The two peaks could be seen over a large background resulting from the Compton of the continuum gamma spectrum arising due to the interaction of thermal neutrons with the <sup>157</sup>Gd. In fact the large cross section of <sup>157</sup>Gd for the thermal neutrons results in a poor photo-peak developed due to the <sup>10</sup>B and <sup>6</sup>Li interaction due to which they cannot be distinguished from the continuum background [171].



Figure 6.4: (a) Pulse height spectrum due toFigure 6.4: (a) Pulse height spectrum dueAlpha particles from Am-Pu source recodedto thermal neutrons from a  $^{252}$ Cf sourceusing LGBOrecoded using LGBO

#### 6.3.2 Scintillation characteristics of LLBO

The optical and electronic properties of LLBO suggested it to be a scintillator for thermal neutrons along with other members of this particular borate family containing lithium and boron. The detectors fabricated from the transparent and crack-free regions of the LLBO have been used to detect alpha rays and thermal neutrons. The pulse-height spectrum due to alpha source emitting energies of 5.2 MeV and 5.5 MeV from an Am-Pu source is shown in Fig. 6.5

(a). It shows a broad peak at  $\sim 170$  channel numbers corresponding to the energies deposited by the alpha particles. The two peaks could not be resolved, though the detection of alpha particles suggested the neutron detection capability when the scintillator will be exposed in a thermal neutron field. The pulse-height spectrum due to thermal neutrons form a thermalised Am-Be neutron source is shown in Fig. 6.5 (b). The Am-Be source has been thermalised with blocks of graphite with approximately a meter length. The PHS shows two peaks at ~ 75 channel numbers and the other one at  $\sim 350$  channel numbers. The peak at the lower channel corresponds to the thermal neutron interaction with the <sup>10</sup>B. The peak due to <sup>6</sup>Li interaction is at roughly 5 times channel number than the peak corresponding to the boron interaction due to the fact that the charged particles generated in the <sup>6</sup>Li interaction  $\binom{4}{2}He, \frac{3}{1}H$  are both light particle and create ionization as compared to only alpha in <sup>10</sup>B which shares a larger kinetic energy [157]. This is the electron equivalent energy which is roughly 5 times larger than the one in the boron interaction.





Be source recoded using LLBO

It could also be seen that the photo-peak efficiency of the <sup>6</sup>Li interaction is very poor as compared to the <sup>10</sup>B interaction. The peak could barely be seen at the higher channel numbers. The relative differences in the counts are mainly due to the isotopic presence of the two isotopes (<sup>10</sup>B around 20% and <sup>6</sup>Li around 7%) in the rare-earth borate matrix and the difference in the cross-section for thermal neutrons (<sup>10</sup>B around 3800 barns and <sup>6</sup>Li around 950 barns). Further, the peak at lower channel number is merged with background contributed from the gamma and the intrinsic background from the lutetium isotope present in LLBO which is reported in lutetium based crystals [151]. The relatively poor gamma separation is also because of the higher effective atomic number of the material due to presence of heavier lutetium in place of gadolinium.

#### 6.3.3 Scintillation characteristics of LYBO

The properties of the LYBO:Ce suggests it to be an efficient and fast scintillator which has been discussed in the earlier chapter. In order to characterize the scintillation properties of the LYBO, detectors have been processed and coupled to the optical sensors. The signal from the optical sensors has been processed to record the pulse-height spectrum. The pulse-height spectra due to alpha particles are shown in Fig. 6.6(a). The graph shows a PHS comparison due to alpha energies among the three borates studied under the same gain settings. It showed a relatively higher pulse-height in the LLBO where the photo-peak due to alpha was much broader as compared to the other two borates. This gives a very poor resolution for the energies even in the range of 5 MeV and hence the pulse corresponding to the thermal neutron interaction was not very clear. The LYBO detector has been further set up in counting mode to measure the response of the detector to the thermal neutrons. The graph in Fig.6.6 (b) shows the measurements done in the Dhruva reactor when the detector is exposed to a neutron beam [170]. It may be seen that when the full beam was open the counts of the detectors was at least 3 times higher than those obtained with the detector wrapped under lead shield. This is due to

the fact that the lead shield scatters a lot of neutrons also. So, the counts correspond to both the neutrons contribution as well as the gamma contribution. Two lead bricks of  $\sim 30$  cms width were used to shield the detector. When the borated rubber was used to shield the neutron beam the counts drops to 100 times lower than the counts obtained with the full beam. This suggests a larger gamma transparency exhibited by the detector.



Figure 6.6: (a) Pulse height spectrum due toFigure 6.6: (b) Response of the LYBOAlpha from Am-Pu source lab sourcedetector to thermal neutrons in Dhruvarecoded using LLBOreactor in the counting mode

The effect of shield has also been studied on the pulse-height spectrum recorded with the LYBO scintillator as shown in Fig. 6.7(a). Two photo-peaks corresponding to the interactions of neutrons with boron and lithium may be seen here. The peak due to boron is closer to the gamma background and hence the lead shield helps improve the resolution of this peak. Both peaks disappear when the detector was covered completely with the borated rubber which confirms the origin of the two peaks being the thermal neutrons [172]. Further, the pulse-height spectra for thermal neutrons from various sources have been recorded under the same gain settings and are shown in Fig. 6.7(b). It shows the two peaks developed at the same location in

the pulse-height spectrum recoded from all these sources. This confirms the interaction mechanism of the scintillator with the thermal neutrons. Once the detection principle has been experimentally established the detector has been calibrated using a standard neutron flux. TheFig.6.8 shows the calibration curve in the pulse-height mode. The pulse-height spectra for the two fluxes of 250n/s/cm<sup>2</sup> and 150n/s/cm<sup>2</sup> have been recorded under identical settings.



Figure 6.7: (a) Effect of Shield on Pulse heightFigure 6.7: (b) Pulse height spectrumspectrum due to thermal neutrons in Dhruvadue to thermal neutrons from variousreactorsource with various flux range

The peaks due to the interaction of neutrons with both boron and lithium appear at a similar channel number with the difference in the counts for the two fluxes. The area under the graphs has been estimated to take the ratio of the two fluxes and was found to be in good agreement with the ratio of incident fluxes.



Figure 6.8: Comparison of standard neutron flux and calibration



Figure 6.9: Pulse height spectrum for background at a site in Dhruva

The efficiency of the detector has been estimated by comparing the measured integrated counts with the actual neutrons falling over the scintillator. The detection efficiency was estimated to be over 70% for the LYBO detector for an area of  $\sim 0.75$  cm<sup>2</sup>. The detector has been used and tested in the flux range from 10n/s/cm<sup>2</sup> to approx10<sup>7</sup>n/s/cm<sup>2</sup> and showed a low dead time because of the fast response of the scintillator. The LYBO detector has also been used to measure the background neutrons at an experimental site to quantify the background neutron flux. The results are shown in Fig.6.9. For this purpose the detector has been calibrated first with the standard neutron flux. Under the shutdown of the reactor the background spectrum has been recorded in the pulse-height mode at the experimental site. Subsequently, when the reactor was operational, the neutron measurements were carried out in the pulse height mode with the identical parameters. Only the <sup>6</sup>Li interaction was taken into account for estimating the area under the graph to compare the neutrons counts with gamma background. A comparison between the area under the graphs for the <sup>6</sup>Li peak at standard neutron flux of 150n/s/cm<sup>2</sup> and the experimental data estimated the neutrons counts to be below 10n/s/cm<sup>2</sup>. It may be noted that this has been established on the basis of the peak due to neutron interaction which could get developed in such a small background. It could only be possible because of the large efficiency of these detectors. The reactor power during the period of experiments was approximately constant. All these results established that LYBO is comparatively a better scintillator for thermal neutron detection as compared to the other two borates [157]. Compact detectors have been further fabricated by mounting LYBO scintillators over SiPM.



Figure 6.10 (a): PHS due to alpha sourceFigure 6.10 (b): PHS due to thermalusing LYBO with SiPMneutrons using LYBO with SiPM

The SiPM offers a gain comparable to those of the conventional PMT but can be operated at much lower voltages and even in the presence of magnetic fields. Hence much compact devices can be made using them. With this idea the measurements have been performed to record the pulse-height spectrum due to both alpha particles and thermal neutrons. The PHS due to alpha is shown in Fig. 6.10 (a) while that due to thermal neutrons is shown in Fig. 6.10 (b). The pulse-height has been recorded by feeding the bare pulse from the SiPM to the MCA. The pulse-height spectrum shows a single peak corresponding to the alpha energies at a channel number of around 70 which could be further separated from the background by optimizing the electronics for the pulse processing chain in the output of the SiPM. The PHS due to thermal neutrons shows a single peak at a channel number of  $\sim 200$  corresponding to the <sup>6</sup>Li (n,  $\alpha$ ) <sup>3</sup>H reaction [157]. The interaction with boron could not be observed due to a low pulse-height from the LYBO and SiPM detector assembly. This suggests that compact detectors could be used in field conditions based on single crystals of LYBO coupled to SiPM. The signal-to-noise

ratio can be further improved by using enriched lithium and with refinement in the electronics to process the SiPM signal.

### 6.4 Conclusion

Single crystals of 0.2% Ce doped Li<sub>6</sub>Gd(BO<sub>3</sub>)<sub>3</sub>, Li<sub>6</sub>Lu(BO<sub>3</sub>)<sub>3</sub> Li<sub>6</sub>Y(BO<sub>3</sub>)<sub>3</sub> have been processed to fabricate scintillators for the detection of thermal neutrons. For this purpose the scintillators were mounted on conventional PMT's and SiPM and the response of the detector for the gamma radiation, alpha particles and thermal neutrons have been recorded. The detectors showed a poor efficiency for gamma rays due to the low effective atomic number and thin size of the crystal used in the experiment. Alpha radiation could be successfully detected using the scintillation based detectors. Further, the thermal neutron detection has been carried out for all the three detectors. It showed peaks corresponding to the <sup>10</sup>B (n,  $\alpha$ ) <sup>7</sup>Li and <sup>6</sup>Li (n,  $\alpha$ ) <sup>3</sup>H reactions with the thermal neutrons. The LYBO based scintillation detector showed a better response over the other two (LGBO and LLBO) scintillation detectors. Finally, the detector based on LYBO has been calibrated and the efficiency of the detector has been estimated by measuring the spectrum from a standard neutron source. The detector has been used to record the response from the thermal neutrons with fluxes in the ranges varying from 10n/s/cm<sup>2</sup> to  $10^7$  n/s/cm<sup>2</sup>. The detector has also been employed to measure the background neutron flux in the nuclear Dhruva reactor where the background neutron flux has been estimate to be as low as 10n/s/cm<sup>2</sup>. Compact detectors based on SiPM have been fabricated and the response of the detectors to alpha particle and thermal neutrons has been recorded. All these experiments suggested that overall LYBO to be a fast and highly efficient scintillator detector for thermal neutrons.

# **CHAPTER7**

## **Conclusion and Future scope of work**

During the course of this thesis, single crystals of LGBO, LLBO and LYBO have been successfully grown to fabricate compact thermal neutron detectors. The single crystals were grown from melts using the Czochralski technique and the growth parameters were optimised to obtain crack-free and bubble-free transparent single crystals. The thermal, structural, optical, electronic and scintillation properties of the material have been extensively studied. The effect of growth ambient was studied to understand the effect of the defect structure on emission properties and scintillation performance. Thermal neutron detectors were fabricated employing scintillators processed from the grown single crystals. The scintillation properties with alpha, gamma and thermal neutrons were studied for all the crystals. The detectors were deployed in the nuclear reactor beam line after characterizing the performance in different thermal neutron flux ranges. Some important results of all these materials are summarised below;

#### Ce doped Li<sub>6</sub>Gd(BO<sub>3</sub>)<sub>3</sub>

Highly transparent and crack-free single crystals of undoped and Ce doped LGBO were grown. It was observed that due to the viscous properties of the melt and the poor thermal conductivities a slow pull rate (~ 0.25-0.7 mm/h) is essential to achieve single crystals of high quality. A moderated rotation rate in the range of 10-15 rpm is needed to ensure the convex shape of the solid-melt interface required for the stable and homogenous growth. Due to the characteristic large super-cooling present in this material, a high temperature gradient was needed during the growth over the melt interface. A thermal gradient of 60°-80°C/cm just

above the melt was found to be optimum. The presence of cleavage plane makes these crystals prone to the cracking and therefore a passive after heater was used above the crucible and around the growing crystal to minimise thermal stresses. The single crystals of LGBO were grown with a cerium concentration varying from 0.1 to 1 molar % and the effects of the cerium concentration on the growth, optical, electronic and the scintillation characteristics were studied. A higher cerium concentration results in a poor transmission of the grown crystal due to the foggy appearance. The excitation and emission characteristics of the LGBO:Ce suggest a potential scintillator due to a matching emission wavelength with PMT and SiPM. The charged particles generated through the interaction of neutron with <sup>6</sup>Li, <sup>10</sup>B and <sup>157</sup>Gd produce sufficient light in the scintillator to process it into the electronic form. The temperature dependent luminescence studies revealed an energy transfer from the Gd<sup>3+</sup> centers to the Ce<sup>3+</sup> centers which consequently affects the decay kinetics of the scintillator and the decay from LGBO:Ce falls in the microsecond range. This is inconsistent with the characteristic feature of the cerium which exhibits a faster decay due to the allowed dipolar transition. Apart from this the interaction of gadolinium (<sup>157</sup>Gd) which has a higher cross-section in comparison to boron (<sup>10</sup>B) and lithium (<sup>6</sup>Li) for the thermal neutrons results in a continuum gamma shower in the energy rage from 1 MeV to 8 MeV. This could not be absorbed in the scintillator due to its low density and mainly produces the Compton background which overrides the pulse-height spectrum having photo-peaks equivalent to 'Q value' of the thermal neutrons interaction with <sup>6</sup>Li and <sup>10</sup>B present in the scintillator. The light output from the LGBO was the highest among the other members of this family but the slow decay kinetics and the continuum gamma showers become a major drawback for this material to be used as a scintillator for thermal neutron detection. Future research may be driven mainly in the direction of using either depleted <sup>157</sup>Gd or using enriched lithium to increase the efficiency of the reaction of thermal neutrons with <sup>6</sup>Li to enable the scintillator to achieve a clean pulse-height spectrum separated from the gamma background.

### Ce doped Li<sub>6</sub>Lu(BO<sub>3</sub>)<sub>3</sub>

Synthesis of single phase  $Li_6Lu(BO_3)_3$  was carried out by mixing and solid state sintering of the constituent oxides (Li<sub>2</sub>CO<sub>3</sub>, Lu<sub>2</sub>O<sub>3</sub> and H<sub>3</sub>BO<sub>3</sub>). However, the thermal properties measured by TG-DTA analysis indicated the presence of large super-cooling. The observed single endotherm in the repeated heating cycle suggested the formation of a single phase material, but the cooling sequence showed multiple peaks corresponding to the freezing of material at different temperatures. The XRD pattern did not show the presence of impurity phases or the presence is out of the detectable limit and confirmed the synthesis of a single phase material. Single crystal growth experiments were carried out from their melts and transparent crack-free small crystals were obtained under optimized parameters. Although the entire crystal ingot could not be obtained as crack-free and the crystal growth yield was low as compared to LGBO and LYBO single crystals. A broad emission peak similar in these borate crystals, peaking at around 400 nm was observed corresponding to the 5d $\rightarrow$ 4f transition from Ce<sup>3+</sup>ions. The luminescence decay profile of the emission at 400 nm due to excitation of cerium centers showed a single exponential decay of about 30 ns. A relatively poor pulse-height spectrum due to the low light yield and the lutetium background due to the presence the Lu-176 radioisotope resulted in a poor discrimination with gamma background present at low channels. During the thermal neutron detection the photo peaks due to <sup>10</sup>B interaction with thermal neutrons could not be well resolved from the low channel background noise. However, the peak due to the <sup>6</sup>Li interaction could be detected.

#### <u>Ce doped Li<sub>6</sub>Y(BO<sub>3</sub>)<sub>3</sub></u>

The Czochralski technique was used to successfully grow single crystals of 0.1% and 0.2% Ce doped  $Li_6Y(BO_3)_3$  from their melts. The growth parameters could be successfully optimized for the growth of highly transparent and crack-free single crystals of LYBO:Ce. The optimized pull

rate was in the range of 0.2-0.5 mm/h for the doped/undoped crystals and the rotation was kept around 10-12 rpm during the entire growth. It is required to provide a high temperature gradient of about 100°C/cm for the stable growth of crystals due to the presence of large supercooling in their freezing behavior. The growth experiments carried out with a lower temperature gradient resulted in the growth of a poor foggy or milky polycrystalline material. The Photoluminescence spectrum showed excitation bands at 310 nm and 350 nm and a broad emission peaking at 420 nm due to the characteristic transitions of the Ce<sup>3+</sup> ions. A fast decay time of about 25 ns was measured that makes this material suitable for the radiation detector applications where high count rates prevail. The temperature dependent emission measurements were performed with the samples grown in air and argon ambient. The results indicates thermal quenching of emission with increase in temperature for samples grown in argon while no such effect was observed for the crystals grown in air. This suggests that the presence of oxygen is favourable to grow these single crystals with lower defect concentrations which are responsible for the thermal quenching. Further, the scintillation decay profile showed difference in the decay time measured for the gamma and neutrons. This is important as it could be helpful to separate gamma interaction from the neutron events using the pulse-shape discrimination technique. Thermal neutron detection measurements carried out using scintillators processed from LYBO:Ce showed two distinct photo peaks corresponding to the <sup>10</sup>B and <sup>6</sup>Li interaction with the thermal neutrons. The pulse-height due to the <sup>6</sup>Li interaction was found to be at channel numbers five times that observed for the boron interaction. It can be assigned to the fact that the lighter charged particles are generated in the interaction with <sup>6</sup>Li having a higher Q value in the scintillator. A compact detector was fabricated using an SiPM as a photo-sensor coupled with the scintillator single crystal for thermal neutrons detection. Further optimization of electronics is in progress to achieve a better pulse-height spectrum from these compact detectors.

#### **Challenges and Scope for Future Studies**

This research work highlighted a comparative study on LGBO, LLBO and LYBO for their thermal, structural, optical and electronic properties to understand their suitability for scintillation application in the detection of thermal neutrons. Some of the challenges associated with the growth of these single crystals could be successfully addressed. However, there are still many unresolved issues which remain unexplored and leave a scope for further studies in future. The different aspects which will be further explored are given below:

- Growth of large size single crystals with higher yields: Crystal growth parameters will be optimized to grow large size (diameters greater than 20 mm) single crystals up to 50 mm diameter and 50 mm length to enhance the crystal growth yield from the total charge. This will further save the cost and the loss of material as the left over charge cannot be used for the second growth due to the selective evaporation of the material and hence the deviation of the stoichiometry in the left over charge. The effect of ambience and their direct observation over defects will be studied. A mix ambience of oxygen and argon will be carried out to minimize the thermal quenching tendency while trying to avoid the oxidation of Ce<sup>3+</sup> ions into Ce<sup>4+</sup> ions which is non-radiative in nature and hence affects the light yield of the scintillator.
- Growth of single crystals with enriched boron and lithium: The growth of single crystals of these families of borates was carried out using a starting material with the presence of natural levels of isotopes for <sup>10</sup>B and <sup>6</sup>Li. It is observed that the efficiency of these detectors for thermal neutrons will increase many folds by growing the crystals from starting material with enriched isotopes. Enrichment is a highly specific job and may not be desirable beyond a certain limit due to the high cost of the detector in that case. Hence to optimize the enrichment level single crystals with enriched isotopic materials will be

grown and their scintillation properties will be further studied as a function of the enrichment. The efficiency curve with respect to enrichment level will be an interesting part to investigate and a reasonable enrichment with larger thickness of the detector can be used in a given application. Though due to gamma response, one need to optimise all these parameters in a given application.

- Use of scintillators in mixed field application: Although the scintillators based on LGBO, LLBO and LYBO showed their capability and better efficiency to detect thermal neutrons, the gamma response was seen to considerably high as compared to gas based conventional thermal neutron detectors. This leaves these scintillators to be tested in various mixed field backgrounds with a range of gamma background and neutron fluxes to quantify the lower limit of the detection for these detectors in the mixed field background.
- Comparison of detector with other conventional detectors in a given environment and evaluating their long-term use: Although the detectors have shown their capability for the thermal neutron detection, their long-term use in extreme conditions like reactors has not been investigated in this thesis. The exposure to long-term radiation may induce some defects having detrimental effect on the characteristics of the scintillator. The nature of the radiation induced effects and their recovery also need to be investigated.
- Pulse-shape discrimination study: As the scintillation decay of LYBO:Ce has shown different decay times for gamma radiation and neutrons, pulse-shape discrimination technique could be used to separate the gamma events from the neutron. The basis of the pulse-shape discrimination is the difference in the decay time and a larger decay time will make the process easy and efficient. Hence, some co-dopant can be used to carry out band gap engineering in order to improve the figure of merit.

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