

To the Graduate Council:

I am submitting herewith a thesis written by Everett M. Cavanaugh entitled "Development of Codoped Cesium Iodide Scintillators for Medical Imaging Applications." I have examined the final paper copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Medical Physics.

Charles Melcher, Major Professor

We have read this thesis
and recommend its acceptance:

Charles Melcher

Michael Howard

Lawrence Heilbronn

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

To the Graduate Council:

I am submitting herewith a thesis written by Everett M. Cavanaugh entitled "Development of Codoped Cesium Iodide Scintillators for Medical Imaging Applications."

I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Medical Physics.

Charles Melcher, Major Professor

We have read this thesis
and recommend its acceptance:

Charles Melcher

Michael Howard

Lawrence Heilbronn

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

Development of Codoped Cesium Iodide Scintillators for Medical Imaging Applications

A Thesis Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Everett M. Cavanaugh

May 2022

© by Everett M. Cavanaugh, 2022
All Rights Reserved.

Acknowledgements

This work was supported by Siemens Medical Imaging.

I would like to thank Dr. Chuck Melcher for his guidance while at the SMRC. His mentorship and advising have helped me grow into a scientist. I am forever thankful for your advising and support through my graduate career. I would like to Dr. Luis Stand for his advising role for my graduate degree. Luis has taught me many important lessons about science and beyond, and I am extremely honored to have studied under him. His guidance and support has been crucial in the development of my scientific skills, and I am forever grateful.

Many thanks to the other graduate students who helped with my training - Matheus Pianassola, Daniel Rutstrom - for always being there to talk about scintillators or classes or science in general. I wouldn't have made it without their help. In particular, I would like to thank Kim Pestovich for her contributions to my projects. We spent many hours in the lab together making measurements, and my project would not be where it is today without her assistance. I would also like to thank Garrett Bennett for his work on the vibration sensor project.

Many thanks to Doug Fielden and Bo Bishop for their excellent technical services throughout the years. Many of my projects would not be possible without their technical knowledge and expertise, and I am grateful for their help in making my ideas reality.

I would like to thank my family for their support of my educational endeavors. I would not be here if it were not for your dedication, love, and support. Thank you for helping me get to where I am today.

Abstract

Cesium iodide has a rich history as a scintillating material. CsI possesses favorable physical characteristics like a high density of 4.51 g/cc and high effective atomic number, however, the undoped compound is not suitable for most radiation detection applications due to low light yield at room temperature. To enhance its scintillation properties, CsI is commonly doped with either Na or Tl, leading to significantly higher light yields than the pure compound. Doped CsI finds use in a variety of fields, but primary applications include radiography, tomography, and geological exploration. However, Na- and Tl-doped CsI scintillators also have severe afterglow that limits their ability to be used in high flux imaging applications, such as computed tomography. Literature reports success in the suppression of afterglow in CsI:Tl through the addition of codopants. Yet, similar work to improve the properties of CsI:Na is unexplored. In this work, the effects of codoping on the light yield and afterglow, among other properties, of CsI:Na single crystals were investigated. Crystals codoped with Eu^{2+} , Yb^{2+} , Sm^{2+} , Sr^{2+} , Ca^{2+} , and Rb^{+} were grown via the Bridgman method and characterized.

Table of Contents

1	Introduction	1
1.1	Scintillators and Radiation Detection	1
1.2	Cesium Iodide Scintillator	5
1.2.1	Physical Properties of Pure CsI	5
1.2.2	Scintillation Mechanisms of CsI:Na	5
1.3	Application of Codoping to Correct Afterglow in CsI:Tl	8
1.4	Thesis Objective	11
2	Experimental Methods	12
2.1	Crystal Growth of CsI	12
2.1.1	Bridgman Crystal Growth	12
2.1.2	Ampoule Selection, Raw Material Preparation, and Pre-synthesis	14
2.1.3	Synthesis and Growth	18
2.2	Characterization Procedures	22
2.2.1	Radioluminescence	22
2.2.2	Light Yield	25
2.2.3	Scintillation Decay Time	27
2.2.4	Photoluminescence	27
2.2.5	Afterglow	29
3	Results	31
3.1	CsI:Na Reference Crystals	31

3.1.1	Crystal Growth and Quality	31
3.1.2	Scintillation Performance of CsI:Na	31
3.2	CsI:Na,Eu Crystals	37
3.2.1	Crystal Growth and Quality	37
3.2.2	Scintillation Properties of CsI:Na,Eu	43
3.3	CsI:Na,Yb Crystals	51
3.3.1	Crystal Growth and Quality	51
3.3.2	Scintillation Characteristics of CsI:Na,Yb	54
3.4	CsI:Na,Sm Crystals	62
3.4.1	Crystal Growth and Quality	62
3.4.2	Scintillation Characteristics of CsI:Na,Sm	62
3.5	CsI:Na,Ca Crystals	71
3.5.1	Crystal Growth and Quality	71
3.5.2	Scintillation Characteristics of CsI:Na,Ca	71
3.6	CsI:Na,Sr Crystals	79
3.6.1	Crystal Growth and Quality	79
3.6.2	Scintillation Properties of CsI:Na,Sr	79
3.7	CsI:Na,Rb Crystals	88
3.7.1	Crystal Growth and Quality	88
3.7.2	Scintillation Properties of CsI:Na,Rb Scintillators	88
4	Conclusions	97
A		108
A.1	Development of an Accelerated Crucible Rotation Technique Mechanism for Vertical Bridgman Growth	108
A.2	Measurement of Vibrations on a Bridgman Furnace	112
Vita		116

Nomenclature

ER	Energy Resolution
LTF	Last to Freeze
LY	Light Yield
STE	Self Trapped Exciton

Chapter 1

Introduction

1.1 Scintillators and Radiation Detection

A scintillator is a material that converts energy from ionizing radiation to visible photons. Scintillators are coupled to a photosensitive device such as a photomultiplier tube or a photodiode to form robust radiation detectors capable of both radiation monitoring and spectroscopy.

Scintillators are used extensively in the fields of high energy physics, geophysical exploration, space exploration, nuclear security, and medical imaging. There are several important properties of a scintillator, and they determine the scintillator's ability to be used in specific applications. These properties are: effective atomic number (Z_{eff}), density, light yield, decay time, afterglow, energy resolution, light yield proportionality, machinability, and low cost of manufacturing.

The density and Z_{eff} determine a material's linear attenuation coefficient and stopping power. The attenuation coefficient is a measure of how well a material can stop X-rays or gamma rays, and the stopping power is a measure of how well the material can stop high energy charged particles. An ideal scintillator has a high Z_{eff} and high density, so that it is able to effectively absorb ionizing radiation and convert the energy into scintillation photons.

Light yield is a measure of how many photons are produced per unit energy deposited into the scintillator. The light yield of the scintillator is a factor in the sensitivity of a detection system. As such, it is important for a scintillator to have a high light yield, regardless of the intended application.

Scintillation decay time is a measure of how fast a scintillator converts deposited energy into scintillation photons. Common commercial scintillators typically release scintillation photons promptly, with common scintillation decay times within the range of 100 - 1000 ns. Ideally, a scintillator releases all of its scintillation photons very quickly, so individual scintillation events are not convoluted with each other.

Afterglow is a measure of the long-lived light emission after X-ray irradiation. It is the result of delayed recombination from unfavorable traps. Afterglow is a limiting factor in high flux radiation environments like computed tomography (CT) and radiography due to ghosting artifacts in images that are difficult to remove computationally. Therefore, an ideal scintillator is one which has very low afterglow.

The energy resolution is a measure of how well a scintillator can determine the energy deposited in the crystal by an ionizing ray. This is important for applications like SPECT, PET, and nuclear security, where knowing the energy of the radiation interacting with the scintillator is very important. Energy resolution is defined as the full-width half-max of a photopeak divided by the centroid of the photopeak, and is reported as a percentage. An improved energy resolution is reported as a low percentage. Scintillators are able to achieve excellent energy resolution of around 2% in the best cases, but common commercial scintillators have an energy resolution on the order of 5-10%.

The radioluminescence spectra of a scintillator is another important feature of a scintillator. The scintillator should have a radioluminescence spectrum that matches well with a photosensor or else the scintillation light will not be efficiently translated into a detectable signal.

The ideal, perfect scintillator has a high light yield, short scintillation decay time, high linear attenuation coefficient, little to no afterglow, high energy resolution,

and has an emission that matches the quantum efficiency of the photodetector. Unfortunately, no such ideal scintillator has been found, and instead, there exists a range of scintillator materials that have only some of these properties. Therefore, there is a compromise between the performance in these categories for the task at hand. For example, in CT, high light yield and low afterglow are required [18]. In PET, the stopping power and energy resolution are more important [18]. In Table 1.1, various scintillator materials and their properties and applications are presented.

Table 1.1: Common scintillators and their properties and applications, adapted from [27]

Composition	Light Yield	Energy Resolution (%)	Primary Decay Time (ns)	Afterglow	Application
NaI:Tl	41,000	6.5	230	14.1% (3ms)[17]	Portal Monitors, SPECT
CsI:Tl	56,000	7.1	800	1% (3ms)[26]	Radiography and CT
CsI:Na	42,000	7.4	630	0.26%(1s)	SPECT and Radiography
LSO:Ce	23,000	7.9	40	-	PET Imaging
LuAG:Ce	23,000	6.5	100[10]	Slow	Radiography
BGO	9,000	9.3	300[22]	-	Astrophysics
CdWO ₄	28,000	6.8	14,000[32]	0.05%(ms)[18]	CT and HEP

1.2 Cesium Iodide Scintillator

1.2.1 Physical Properties of Pure CsI

CsI scintillators are a species of alkali halide crystal with a Pm-3m (221) primitive cubic structure [34], a Z_{eff} of 54.0, and a density of 4.51 g/cc [28]. These qualities enable large volume growths, [34] and make the material an excellent ionizing radiation absorber [4]. CsI is easily machinable, due to its softness, plasticity, and relative moisture stability compared to other metal halide scintillators [18]. The band gap of CsI is approximately 6.2 eV [20], which enables relatively efficient conversion between deposited energy and scintillation photons with a theoretical maximum light yield of 107,000 ph/MeV [35].

The physical properties of CsI are favorable for a wide range of radiation detection applications [18] [11]. However, CsI does not scintillate efficiently at room temperature, where the light yield falls below 5,000 ph/MeV [2]. The inefficiency at room temperature limits the use of pure CsI to use at temperatures below 100 K like in systems at CRESST [3]. As a result, Cesium Iodide has been doped with a number of activators that stabilize the scintillation performance at room temperature. The two most common dopants for CsI are Tl and Na.

1.2.2 Scintillation Mechanisms of CsI:Na

The scintillation process consists of major phases: energy deposition, thermalization, trapping, and relaxation. In the energy deposition phase of the scintillation process, free electrons and holes are created. In CsI and other alkali halide crystals, the free holes become self-trapped and are referred to as V_k centers. The V_k centers are stable at low temperatures and combine with thermalized electrons to form self-trapped excitons (STE) [13]. Due to the stability of the V_k center at low temperatures, the resultant STE has a very high probability of relaxing radiatively [19]. At higher temperatures, the V_k center becomes unstable and is more likely to recombine with a

thermalized electron non-radiatively. It was found that V_k centers can be stabilized at room temperature by the addition of an impurity that decreases the mobility of V_k centers. The result of this discovery was two commercially viable scintillators that operate efficiently through a wide range of temperatures: CsI:Na and CsI:Tl [23] [33].

CsI:Na was discovered in the mid 1960's and was of great interest due to its improved performance over one of the oldest and most widely used scintillators; NaI:Tl [14]. The exact scintillation mechanism of CsI:Na was not well understood, and several mechanisms were proposed [21]. However, work performed by Ong et al. in 1979 demonstrated that the most probable scintillation pathway for CsI:Na was a Na-localized STE [23]. This model is shown in Figure 1.1, where migratory V_k centers are trapped near a substitutional Na^+ site until a thermalized electron reaches the Na-localized V_k center. The electron will become loosely bound with the V_k center and form an STE that is localized to the Na^+ site. The result of localization around Na^+ site is radiative excitonic emission with a slightly decreased energy when compared to the STE in undoped CsI. The decreased energy of the emission results in a higher wavelength, pushing the emission into the visible range.

This process is relatively efficient, with the light yield of doped CsI at room temperature reaching anywhere from 30-90% of undoped CsI light output at liquid helium temperatures [24] [35]. However, the introduction of substitutional ions also introduces a trap that is known to cause afterglow that is detrimental to its performance in high speed radiography or CT [25].

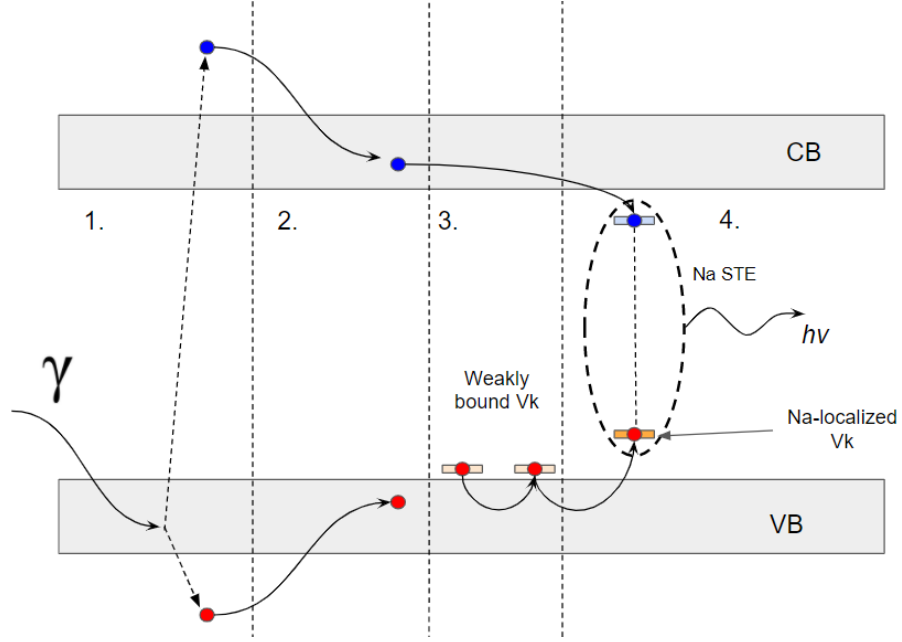


Figure 1.1: Band structure diagram of Na assisted STE relaxation in CsI in four phases. Phase 1 is the ionization phase, where energy is imparted to the crystal and electrons and holes are created. Phase 2 is the thermalization phase, where electrons and holes interact with the lattice and release energy. Phase 3 is where holes become self trapped. At room temperature, V_k centers migrate around the crystal until they encounter a substitutional Na ion wherein they enter phase 4. During phase 4, the V_k center is localized around the Na ion, and interacts with an electron forming an STE. This STE then relaxes radiatively.

1.3 Application of Codoping to Correct Afterglow in CsI:Tl

The scintillation mechanism of CsI:Tl is analogous to that in CsI:Na. Like Na^+ , Tl^+ is an cation that mediates V_k and electron recombination in the CsI host. In CsI:Tl, shallow electron traps around the Tl^0 sites are believed to be the cause of afterglow [5]. Due to the favorable properties, namely its high light yield of 54,000 ph/MeV, extensive work has been done to eliminate the effect of harmful, afterglow-inducing shallow traps.

One of the first attempts to improve the afterglow of CsI:Tl by codoping was published by Brecher et al. in 2005 [7]. In their work, CsI:Tl was codoped with a number of different codopants which includes O, Ca, Ba, K, Na, F, and Br. They observed that the addition of other impurities had an effect on the afterglow and scintillation properties, and that more work should be done with exploring the effects of codoping on CsI:Tl. The same researchers published another study in 2006 about the effects of codoping with EuI_2 [8]. The result of adding EuI_2 was a substantial reduction in the afterglow of CsI:Tl. Thermoluminescence measurements from this study indicate that the Eu^{2+} acts as an electron scavenger that captures electrons before they are trapped at a Tl^+ site. The improvement in afterglow came at a cost, however, in that the light yield of CsI:Tl was severely suppressed. Nevertheless, the hunt for the most effective codopant was launched, and a flurry of activity surrounding CsI:Tl codoping began.

Aside from Eu codoping, it was found that Sm^{2+} , Yb^{2+} and Bi^{3+} also had significant effects on the afterglow properties of CsI:Tl [26] [31] [5] [35]. Each of these added impurities decreased the afterglow of CsI:Tl by an order of magnitude, but every codopant besides Yb had a detrimental effect on the light yield. The case of Yb codoping is quite interesting, as Wu reports that the light yield of CsI:Tl,Yb (98,000 ph/MeV) is close to the theoretical limit for light yield of CsI (110,000 ph/MeV) [35].

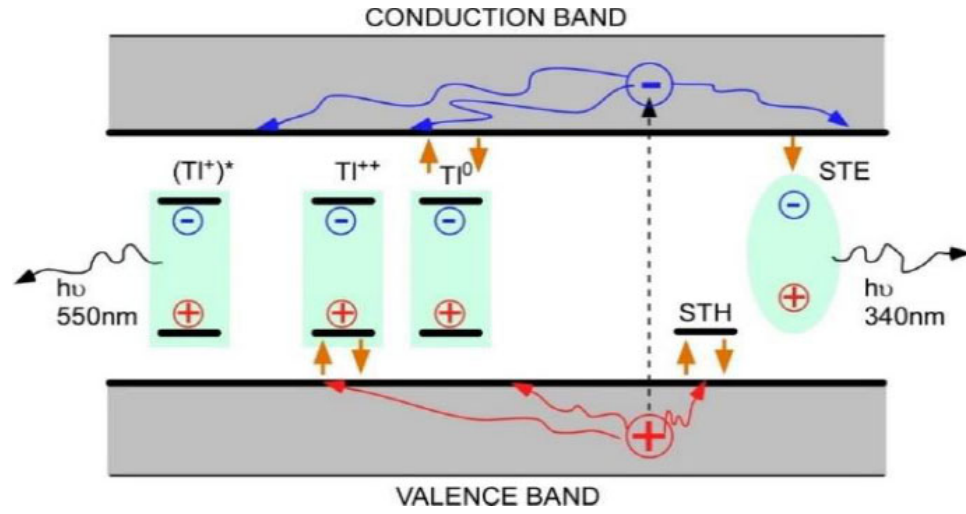


Figure 1.2: Diagram of the scintillation process for CsI:Tl as presented in [5]

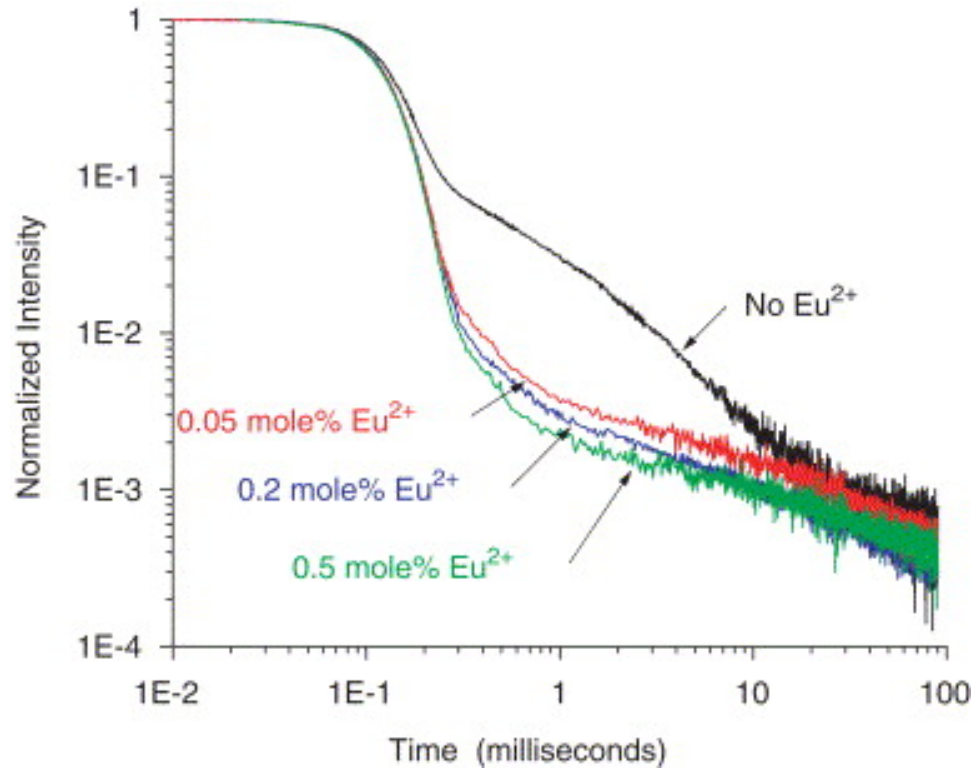


Figure 1.3: Effect of addition of Eu²⁺ to CsI:Tl on afterglow [8].

1.4 Thesis Objective

Such success with codoping CsI:Tl poses the question of whether CsI:Na can have similar improvements made to its scintillation performance via codoping. Codoping CsI:Na with Eu^{2+} and In^+ has been found to improve the light yield of CsI:Na [15]. Some interesting work has also been done with codoping CsI:Na with ^{133}Ba in an effort to provide a steady self-activity signal for detector calibration [16]. There has also been work with introducing CO_3 as a codopant for CsI:Na crystals [9]. Aside from these studies, other codopants have not been extensively explored.

The objective of this study is to explore the effects of cation codoping on the scintillation properties of CsI:Na. Codoped CsI:Na crystals were grown by the Bridgman method, and their scintillation properties were characterized. The codopants studied in this report are Eu^{2+} , Yb^{2+} , Sm^{2+} , Ca^{2+} , Sr^{2+} , and Rb^+ . The scintillation properties of interest are the scintillation light yield, afterglow, and luminescence phenomena.

Chapter 2

Experimental Methods

2.1 Crystal Growth of CsI

2.1.1 Bridgman Crystal Growth

The growth method of choice for metal halide crystals is the Bridgman crystal growth method. With this growth method, a charge (mixed raw material) is placed into a quartz ampoule and then placed into a furnace with at least two independently controlled zones. The top zone is referred to as the hot zone, and the bottom zone is referred to as the cold zone. The hot zone is typically set to a temperature that is above the melting point of the charge, and the cold zone is set to a temperature below the melting point of the crystal, resulting in a controlled thermal gradient. During growth, the crystal is moved through the thermal gradient at a rate of several millimeters per hour. Movement through the thermal gradient allows for the controlled solidification of the charge. It is beneficial to have a sharp thermal gradient [29], but sometimes a furnace is unable to achieve sharp gradients due to convective airflow. To insulate the two zones from each other and improve the thermal gradient, an insulating diaphragm is placed between the hot and cold zones.

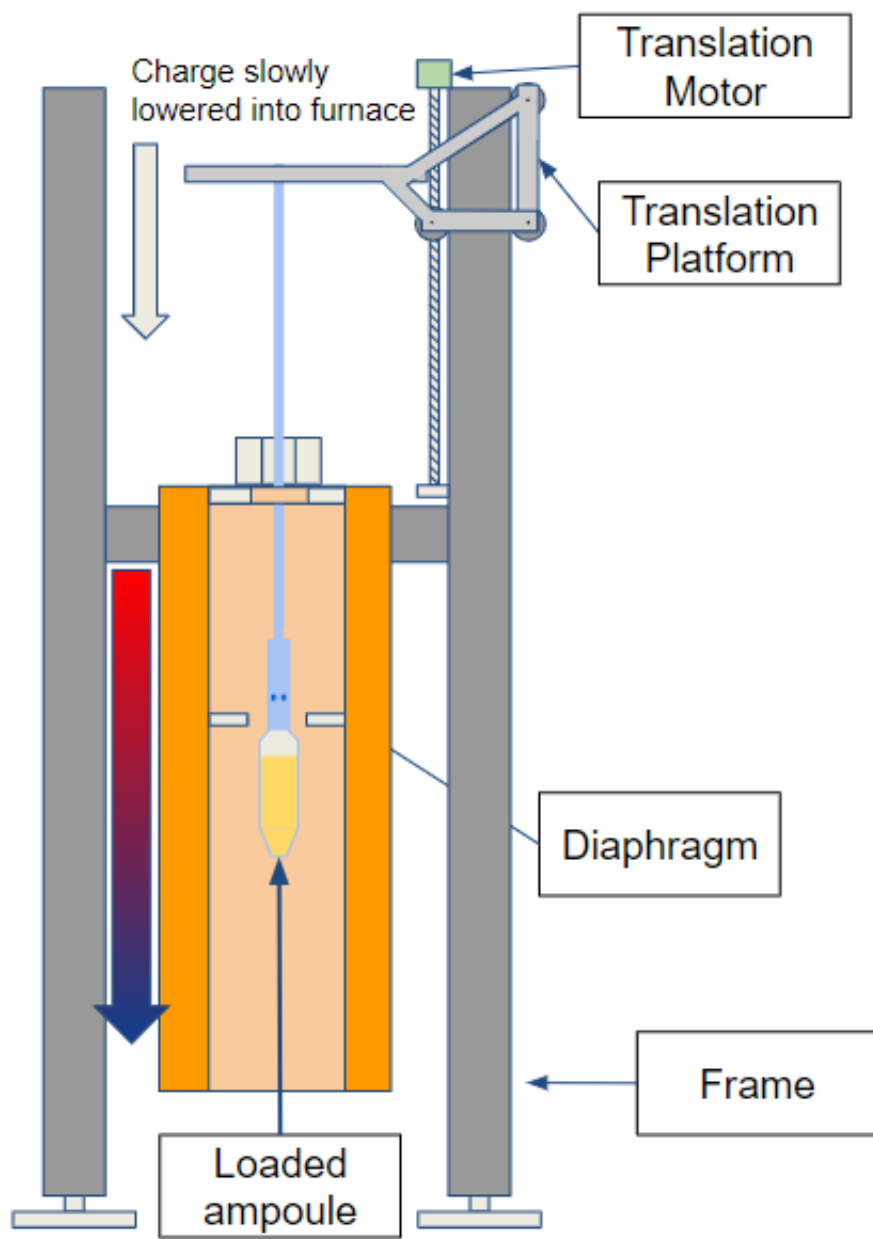


Figure 2.1: Diagram of Bridgman furnace at the Scintillation Materials Research Center

2.1.2 Ampoule Selection, Raw Material Preparation, and Pre-synthesis

The precursor compounds for the cesium iodide scintillators are hygroscopic. Therefore, special material storage and charge containment are required. An evacuated quartz ampoule is the growth container commonly used for Bridgman growth of halide scintillators, as it has a low thermal coefficient of expansion, high softening point, and is relatively inert. However, some materials are unable to be grown in quartz ampoules, due to reactivity of the charge with the quartz. A well-known material that cannot be grown in conventional quartz ampoules is NaI:Tl. NaI:Tl crystals create chemical species that are corrosive to quartz [30], and NaI crystals grown with bare quartz pose an ampoule breakage hazard, in addition to producing low-quality crystals due to either extensive cracking or impurity diffusion.

The solution to growing corrosive metal halides in quartz is the addition of a thin layer of carbon to the interior of the quartz ampoule. The carbon coating serves two purposes. The first of which is to shield the quartz from the corrosive materials. The second purpose is reduction of radical diffusion into the melt, as the carbon acts as a OH^- scavenger [30].

For this experiment, we are using NaI as dopant. Due to the similar chemical nature of CsI and NaI, the CsI:Na crystals were grown in carbon coated quartz ampoules out of an abundance of caution. Additionally, growth in the carbon coated ampoules offered the benefit of possible reduction in impurity contamination from the quartz. These ampoules were 12 mm in diameter and 100 mm tall, with a 15 mm length cone for seeding. The cubic structure of the CsI lattice facilitates crystal growth, so a grain-selecting capillary was not used. These carbon coated ampoules were manufactured by Sandfire Scientific. Raw materials were weighed out according to table 2.1.2 and loaded into the ampoules while working inside a glovebox.

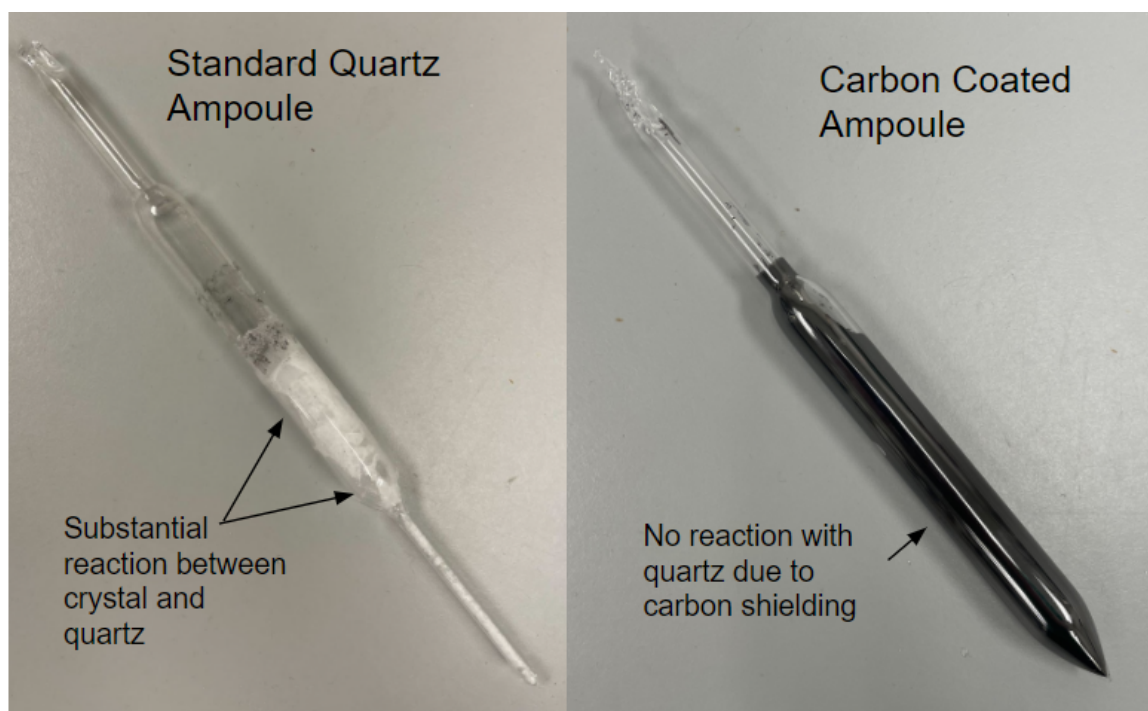


Figure 2.2: Left: Un-coated quartz ampoule. Right: carbon coated quartz ampoule.



Figure 2.3: [1]: ampoule loading glovebox. [2]: Ampoule on vacuum station. [3]: Ampoule being baked out under vacuum. [4]: Ampoule being sealed with a hydrogen oxygen torch.

Table 2.1: Raw material manufacturer, purity, and form. The units of purity are reported in % purity (5N = 99.999% pure)

Raw Material	Manufacturer	Purity	Form
CsI	APL	5N	Beads
NaI	APL	5N	Beads
EuI ₂	Sigma Aldrich	4N	Beads
YbI ₂	APL	3N5	Powder
CaI ₂	APL	4N5	Beads
SrI ₂	APL	4N5	Beads
SmI ₂	APL	4N	Powder

Table 2.2: Raw material charges for each crystal grown as a part of this study. All units reported in grams.

Composition	CsI	NaI	EuI ₂	YbI ₂	SmI ₂	SrI ₂	CaI ₂	RbI	Total Charge Mass
CsI:Na	19.965	0.035	-	-	-	-	-	-	20.000
CsI:Na,Eu(0.3,0.5%)	19.809	0.035	0.156	-	-	-	-	-	20.000
CsI:Na,Eu(0.3,0.1%)	19.934	0.035	0.031	-	-	-	-	-	20.000
CsI:Na,Eu(0.3,0.01%)	19.962	0.035	0.003	-	-	-	-	-	20.000
CsI:Na,Yb(0.3,0.1%)	19.932	0.035	-	0.033	-	-	-	-	19.999
CsI:Na,Yb(0.3,0.01%)	19.963	0.035	-	0.004	-	-	-	-	20.001
CsI:Na,Ca(0.3,0.3%)	19.897	0.035	-	-	-	-	0.068	-	20.000
CsI:Na,Ca(0.3,0.01%)	19.963	0.035	-	-	-	-	0.002	-	20.000
CsI:Na,Sm(0.3,0.1%)	19.934	0.035	-	-	0.031	-	-	-	20.000
CsI:Na,Sm(0.3,0.01%)	19.962	0.035	-	-	0.003	-	-	-	20.000
CsI:Na,Sr(0.3,0.1%)	19.939	0.035	-	-	-	0.026	-	-	20.000
CsI:Na,Sr(0.3,0.01%)	19.965	0.035	-	-	-	0.003	-	-	20.002
CsI:Na,Rb(0.3,0.1%)	19.949	0.035	-	-	-	-	-	0.016	20.000
CsI:Na,Rb(0.3,0.01%)	19.964	0.035	-	-	-	-	-	0.002	20.000

The glovebox maintains an atmosphere with 1-4 ppm of O_2 and less than 1 ppm of H_2O . After removal from the glovebox, each ampoule was immediately attached to a vacuum system. Once secured to the vacuum system, the ampoule was evacuated, and internal air pressure of the ampoule is brought to 50 μ torr. A rolling clam-shell furnace was closed around the ampoule and heated to 250°C for 2 hours. Then, the ampoule was sealed under vacuum by using a hydrogen-oxygen torch.

2.1.3 Synthesis and Growth

The first step in the crystal growth process is the melting and synthesis phase, where the raw materials are melted and mixed via convective flows. In the synthesis phase, it was crucial for the furnace temperature to exceed the melting point of all melt constituents. If the melting point of all constituents is not exceeded, the unmelted constituent will not mix into the bulk melt, yielding a compositionally non-uniform crystal. In Figure 2.4, thermal profiles that were measured by passing a thermocouple along the length of the Bridgman furnace are presented. During the beginning of the project, the "Old Profile" was used, and poor quality crystals were grown as a result. The thermal gradient was measured, and the temperature was found to be below the melting point of NaI, which lead to the Na dopant being non-uniformly distributed through the boule. In Figure 2.5, we compare the pulse height spectra of two crystals; one synthesized and grown in an unsuitable thermal gradient, and another grown in a suitable thermal gradient. Despite the crystals having little visible difference, there exists a severe difference between the pulse height spectra. It can be seen in the pulse height spectra that the "photopeak" in the poorly synthesized sample is actually a continuum of many individual photopeaks summed into one. On the contrary, the crystal that was synthesized and grown in a suitable gradient has a single photopeak. Given these results, the thermal gradients for all crystal growths was chosen to have a synthesis section at +40°C above the melting point of the crystal to ensure adequate incorporation of all melt constituents.

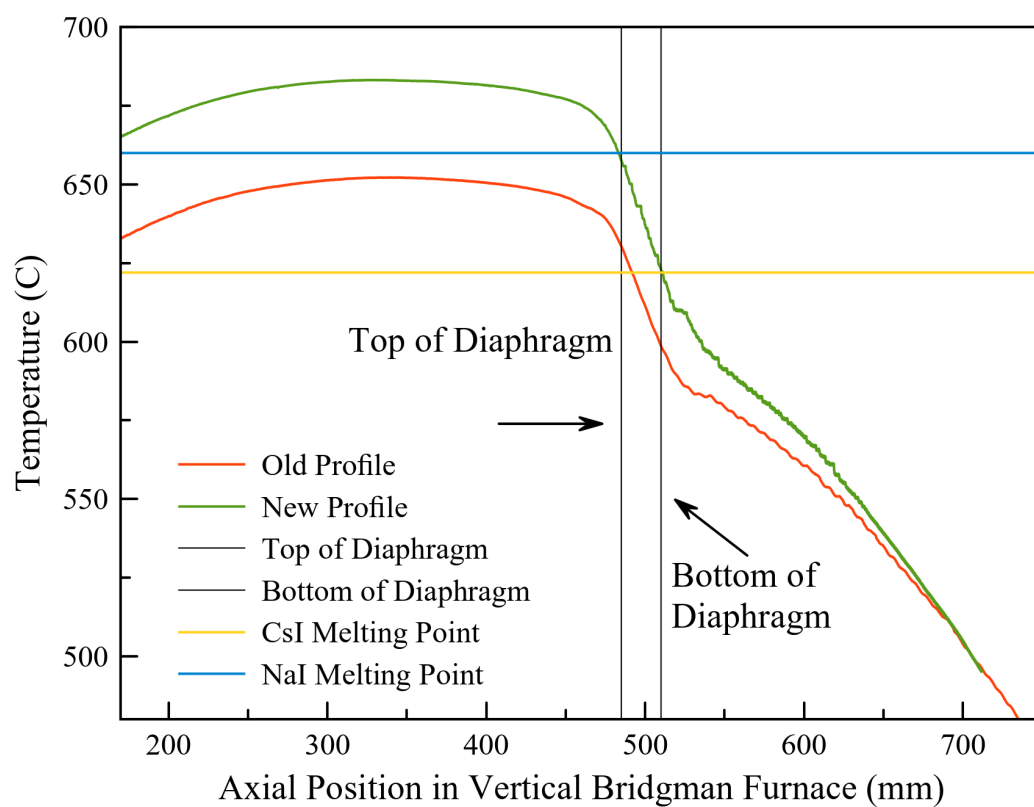


Figure 2.4: Three zone Bridgman furnace thermal profiles

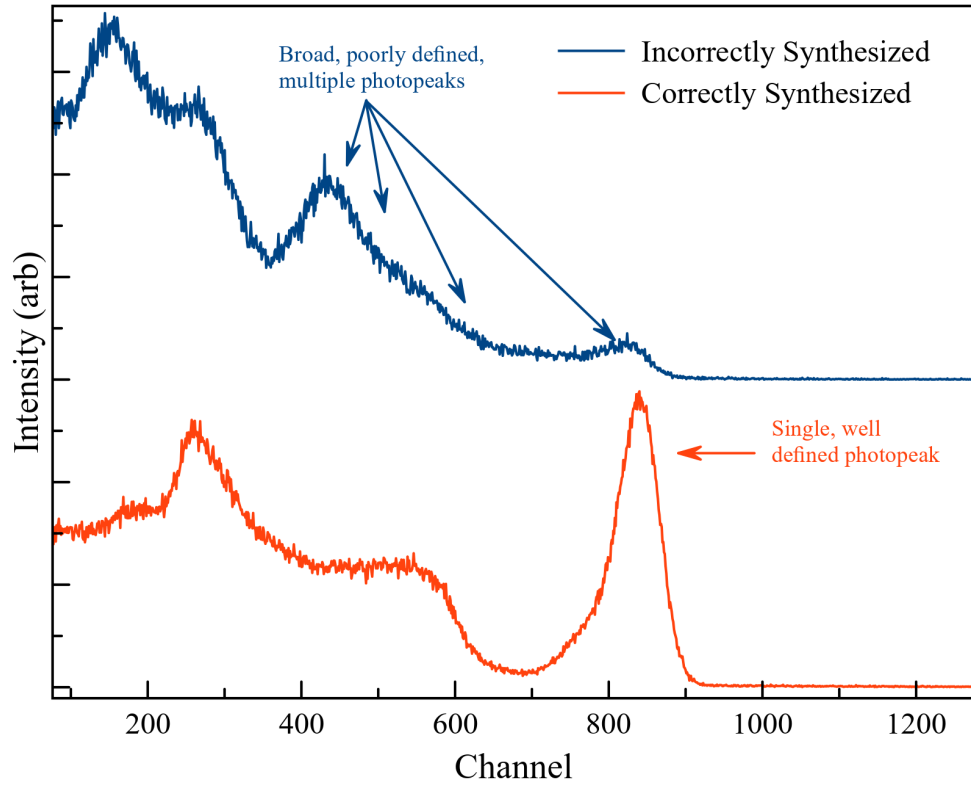


Figure 2.5: Pulse height spectra of two CsI:Na(0.3%) crystals grown with different thermal gradients.

Crystal Growth Procedure

For crystal growth of the codoped CsI:Na crystals, there were two methods used. The first method is the singular crystal container growth, where the ampoule containing the charge is placed in a small-diameter quartz boat. The boat is then lowered into a vertical Bridgman furnace and placed at a point just above the diaphragm of the furnace. The second method is the multi-crystal container growth, wherein 7 to 9 ampoules are loaded into a large diameter quartz boat and placed into a large bore vertical Bridgman furnace. In both cases, the compounds are melt-synthesized at a temperature as determined by the highest constituent melting point. Then, the temperature of the lower zone was decreased to create the optimal thermal gradient. After equilibrating, the ampoules were then translated at a rate of 2-3 mm/hr through an insulating diaphragm located between the hot and cold zones of the furnace.

The multi-crystal growth approach provides an advantage of being able to rapidly grow 9 crystals in the time that it takes one crystal to grow on its own in a single crystal growth. The speed at which crystals can be grown is an important aspect to codoping projects, as it allows for wider screens of codopant species and concentrations to be performed as the experimenter is no longer as limited by the crystal growth rate of one single crystal. There exist drawbacks to this method of crystal growth, which are mainly attributed to the loss of a uniform radial thermal gradient due to the insulating nature of the quartz ampoules of which the samples are grown within and the geometry of the sample packing. Evidence of a non-uniform radial thermal gradient can be observed in the crystal quality section with impurity-rich regions on one side of the boule.

Crystal Sample Preparation

Once crystals are extracted from their ampoule, the samples must be processed into a form fit for characterization. In the beginning of the project, the samples were cut into two 12 mm diameter by 20 mm height crystals, but there were suspicions of axial

dopant segregation. In order to investigate the possible effects of dopant segregation in the crystal on scintillation properties, the crystals were cut into six 12 mm diameter 4 mm thick slabs as shown in Figure 2.6. Crystals were cut using a diamond wire saw with mineral oil as a lubricant. The cone section of the crystal was cut 1 mm above the end of the taper. Once the crystals were cut down to size, each slab was polished using 600, 800, and then 1200 grit SiC polishing pads in sequential order. The result was a clear, mostly scratch-free crystal that was of a good optical quality.

2.2 Characterization Procedures

The Scintillation Materials Research Center has a suite of characterization equipment that is used to characterize scintillation properties of a wide range of materials. The characterization lab has equipment capable of measuring scintillation light yield, scintillation decay time, energy resolution, radioluminescence and photoluminescence.

2.2.1 Radioluminescence

Radioluminescence measurements are carried out in a leaded light-tight box with an X-ray tube, monochromator, and photosensor. The sample is placed within the beamline of the X-ray generator and is irradiated continuously. The scintillation light then passes through the monochromator, and is detected by a photosensor. The resulting data is a plot of wavelength of scintillation light versus intensity at that particular wavelength. Radioluminescence measurements can be performed using one of two geometries; the transmission mode and the reflection mode. Transmission mode is the more repeatable method of measuring radioluminescence and works well for measuring transparent samples. The reflection mode is good for measuring opaque samples or samples where self absorption is expected. Reproducibility was important for this experiment, so the transmission geometry was selected. A diagram for this measurement setup is shown in Figure 2.7.



Figure 2.6: Diagram of cut crystal

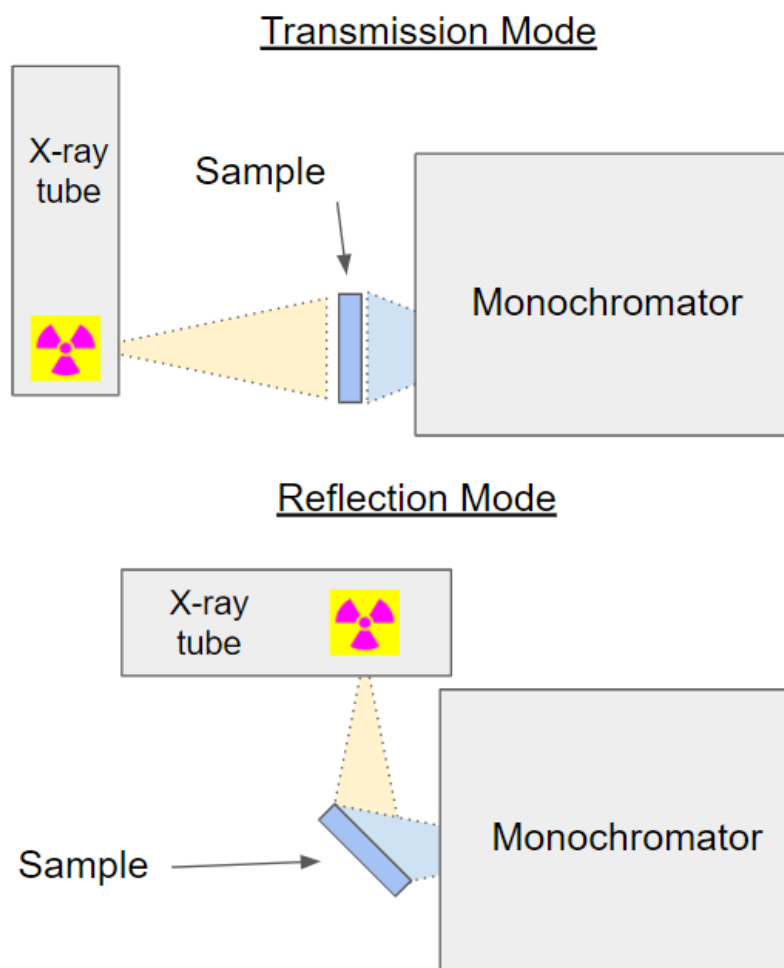


Figure 2.7: Diagram of radioluminescence setups

2.2.2 Light Yield

The light yield of a scintillator is measured using the single photoelectron technique described in [12]. The technique requires several measurements to be made. The first step is to calculate the integral quantum efficiency of the scintillator and PMT by convolving the radioluminescence spectrum of the sample with the quantum efficiency of the photomultiplier tube. This is carried out using equation 2.1; where i is the wavelength, C_i is the radioluminescence count at wavelength i obtained through the procedure outlined in Section 2.3.1, and $QE(i)$ is the photomultiplier quantum efficiency at wavelength i .

$$IntegralQ.E. = \frac{\sum_{200}^{800} C_i \cdot QE(i)}{\sum_{200}^{800} C_i} \quad (2.1)$$

After the integral QE is collected, the spontaneous single photoelectron (SPE) is measured. In this measurement, a bias of 1500 V is applied to the PMT, and the spectroscopy amplifiers are set to maximum gain. Spontaneous photoelectrons are released by the photocathode, which cause a signal from the PMT. This signal is amplified and read by a microchannel analyzer (MCA), and the centroid is recorded.

After the SPE centroid has been recorded, the sample can be measured. The sample is placed in the setup as described in Figure 2.8. The PMT bias is then switched on, and the pulse height spectrum is measured. The centroid of the photopeak is recorded, and the sample is removed from the housing.

The light yield of the sample is calculated according to 2.2, where E_γ is 662 keV from the Cs-137 source, PP_{ctr} is the centroid of the sample, and the parameters α and β are gain constants.

$$LY = \alpha PP_{ctr}^{E_\gamma} * \left(\frac{\beta}{SPE_{ctr}} \right) * \frac{1}{E_\gamma * IntegralQ.E.} \quad (2.2)$$

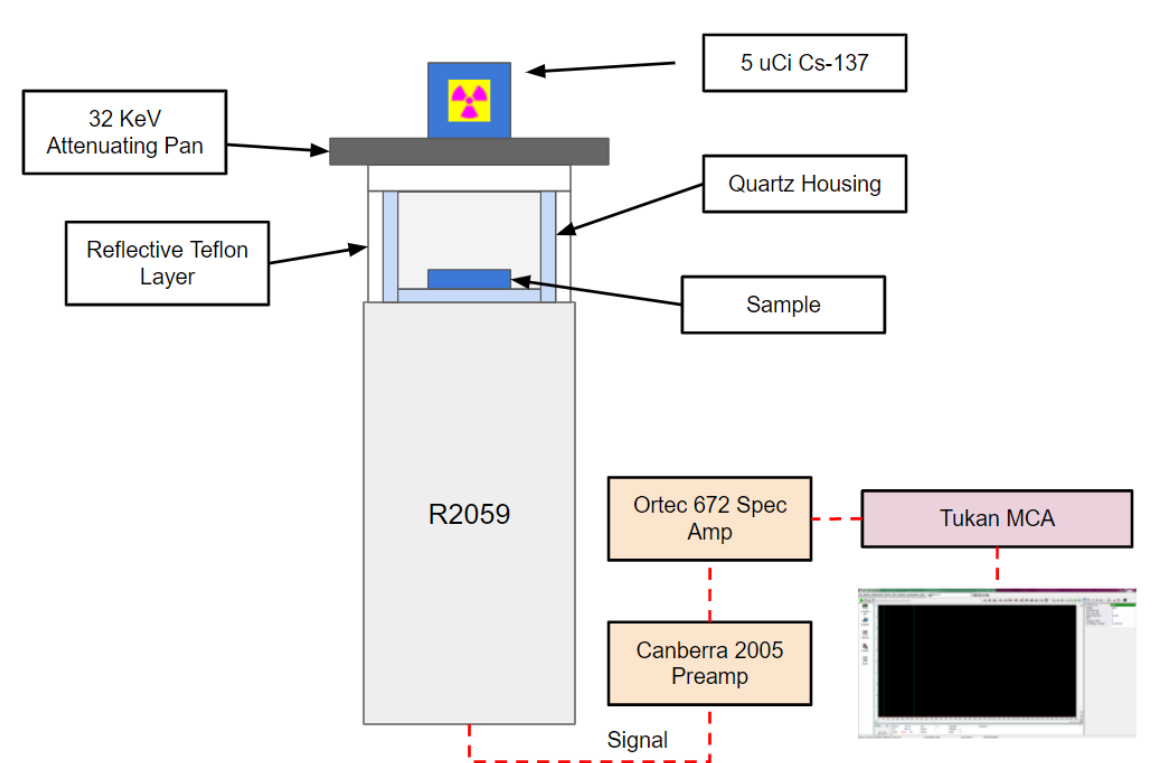


Figure 2.8: Diagram of pulse height spectra setup.

2.2.3 Scintillation Decay Time

The scintillation decay time was measured by a method outlined by Thomas and Bollinger [6]. In this setup, two PMTs are utilized to create a stop and start signal. These signals are fed into a pulse processing chain and outputs a pulse with a height corresponding to the time between start and stop pulses. These pulses are read and sorted by a Tukan 8k MCA and plotted in its software.

2.2.4 Photoluminescence

Photoluminescence is a measurement where optical centers are excited by ultraviolet light, and the emissions from that luminescent center are measured. The photoluminescence measurements are performed with a Horiba Jobin Yvon Fluorolog using a xenon lamp. There are three distinct ways to measure photoluminescence properties of scintillator crystals, and they are measurements in emission mode, excitation mode, and 3D mode.

For the emission measurement mode, an excitation wavelength is chosen and modulated by a monochromator located in front of the lamp, and the emissions from the scintillator are measured using a scanning monochromator placed in front of a photomultiplier. Excitation operates very similarly, but instead of the emission monochromator scanning, the excitation monochromator scans. These measurements are relatively fast, efficient, and precise, but require knowledge about the emission spectrum before making the measurement. This prior knowledge can be obtained through radioluminescence measurements, but in many cases, may not be sufficient for a thorough study. The 3D measurement requires no prior knowledge of the emission and excitation spectra, but it takes significantly more time to measure. To reduce the time spent measuring a sample, the spectral resolution is decreased. Areas of interest located by a 3D emission excitation profile can be inspected further by a finer resolution excitation scan or emission scan.

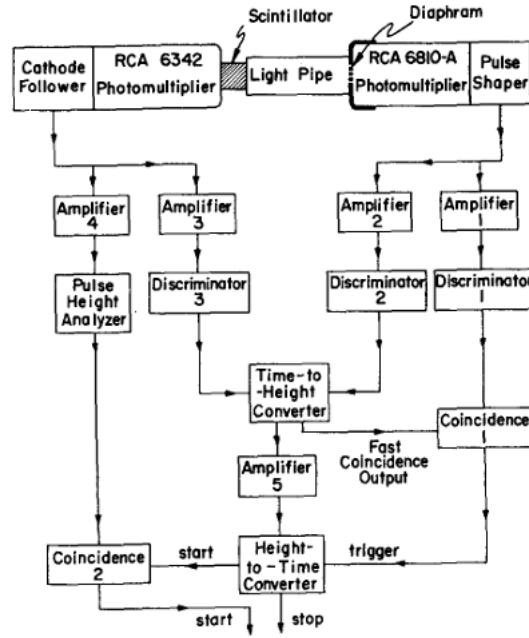


Figure 2.9: Bollinger Thomas pulse processing chain for measuring scintillation decay time [6]

2.2.5 Afterglow

Afterglow is a measure of the phosphorescence, or long lived luminescence of the scintillator. The afterglow of the scintillator samples are measured using an R2059 PMT operating in current mode. The PMT signal is fed into an amplifier that converts the PMT current into a signal ranging from 0 to 10 V. This signal is then read into an analog to digital (ADC) converter connected to a computer running LabVIEW. The custom LabVIEW program samples the ADC at a rate of 48 kHz, which allows measurements of the PMT current every 20 μ s. The sample is irradiated by an X-ray tube with a tungsten target at a tube voltage of 35 KV and a current of 0.1 mA for 5 minutes. An X-ray shutter should be used for this measurement as well, since the X-ray is not pulsed. However, the X-ray shutter in the SMRC was inoperable at the time of measurement so it was not used.

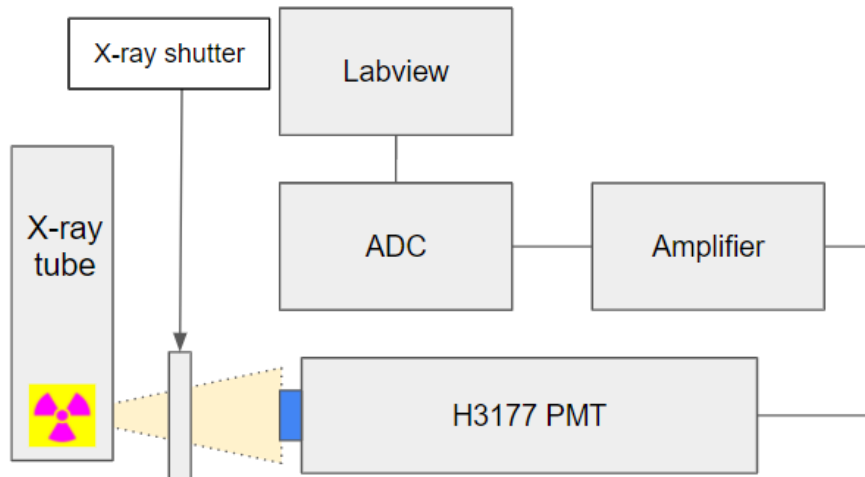


Figure 2.10: Experimental setup for afterglow at the SMRC

Chapter 3

Results

3.1 CsI:Na Reference Crystals

3.1.1 Crystal Growth and Quality

For a consistent comparison, a CsI:Na reference crystal was grown. The reference crystal was grown, processed, and characterized in the same way as the codoped CsI:Na samples. The melt concentration of Na was chosen to be 0.3 mol% because it had yielded the best quality crystals with consistently high light yield. The reference crystal is shown in Figure 3.1, and was colorless, clear, and of good optical quality. There were no visible inclusions, with the exception of a thin black layer on the last-to-freeze section of the crystal. The black discoloration observed on the last to freeze section is a thin layer of carbon that detached from the walls of the ampoule and floated on the top of the melt during growth. The slabs cut from this boule were also of excellent optical quality, with no evidence of impurities or inclusions throughout the crystal.

3.1.2 Scintillation Performance of CsI:Na

The radioluminescence plot of the CsI:Na reference is shown in Figure 3.2.

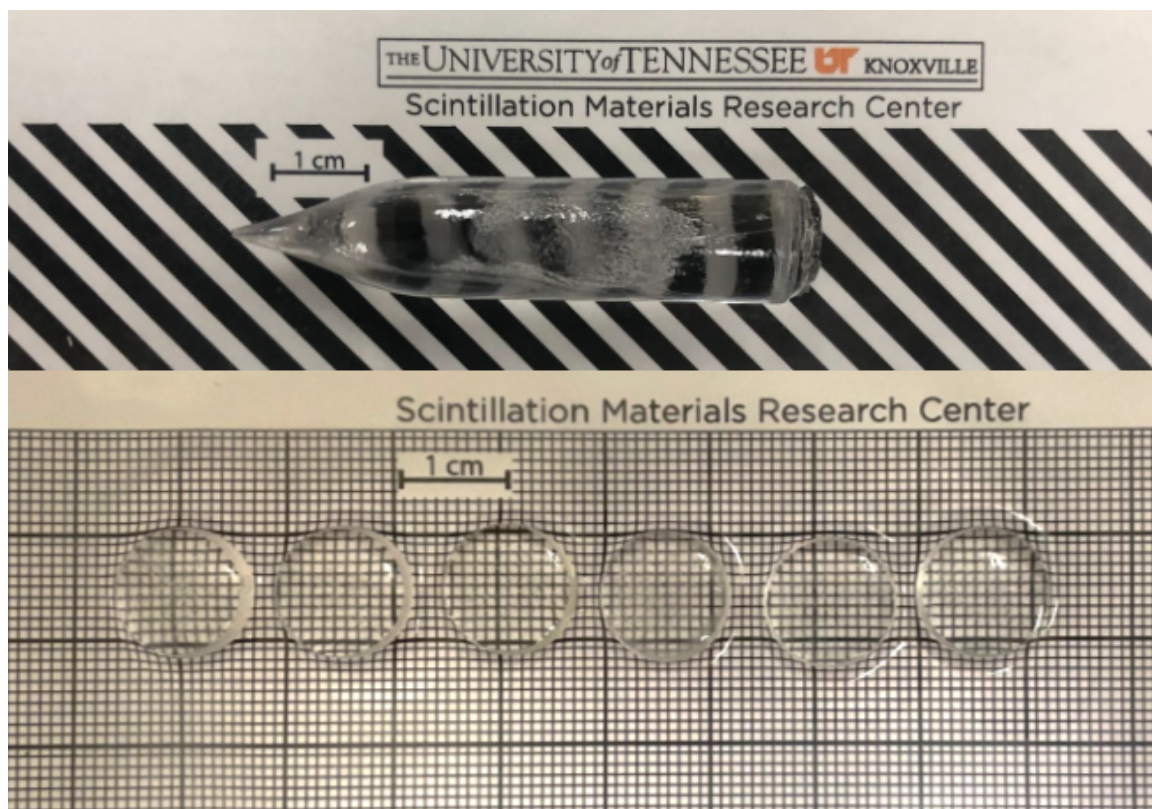


Figure 3.1: Top: Boule after extraction from ampoule. Bottom: Boule sliced into six 4 mm slabs for characterization with slices ordered left to right in ascending order

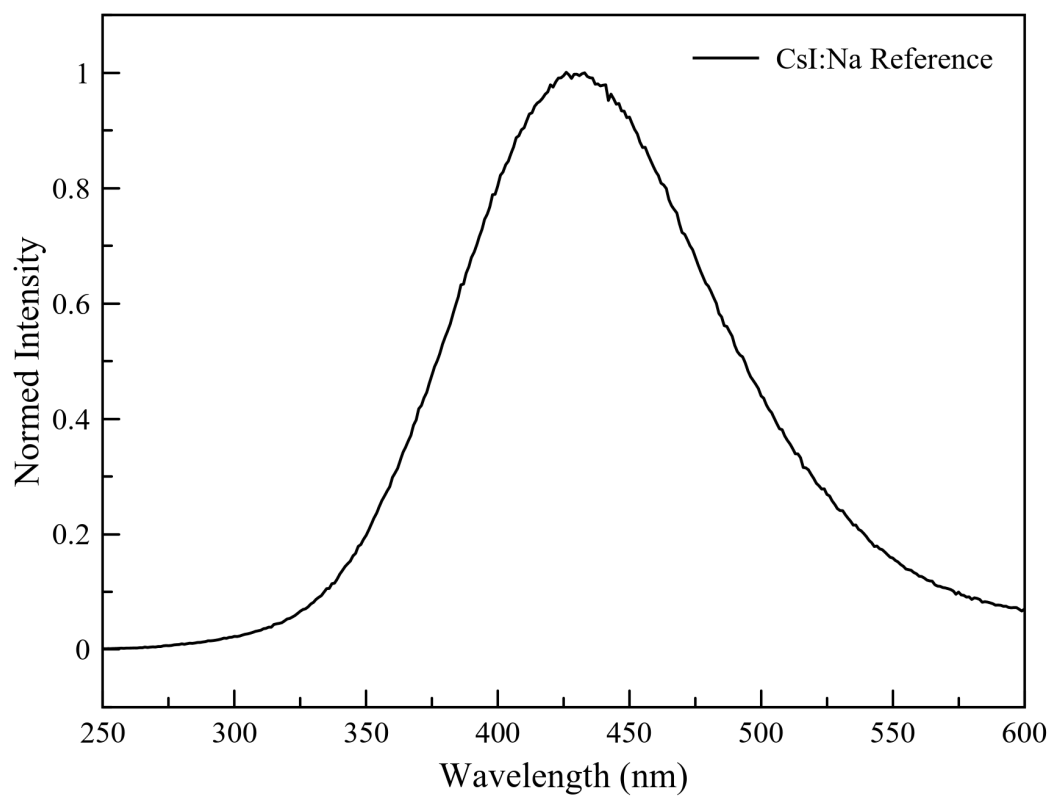


Figure 3.2: Light yield measurements and pulse height spectra of the CsI reference.

The results are in agreement with literature [36] as the radioluminescence emission of these samples is broadband and centered around 425 nm. This result is consistent with Na-localized STE relaxation. The light yield measurements of the reference crystal are shown in Figure 3.3. The pulse height spectra are plotted on the left and demonstrate the spectroscopic quality of the samples. The centroid of the photopeak was used to calculate absolute light yield. The error bars on the absolute light yield plot are representative of measurement error. This error was found by making a measurement of a single slice 21 times and taking the standard deviation of the centroids of the photopeak. The standard deviation in the light yield measurement was found to be 250 ph/MeV. It was assumed that this error propagated across all light yield measurements. It is important to note that this determination of error only accounts for variations in measurement setup, and does not account for variations in sample polishing and handling. Variations in sample setup include positioning of sample on the PMT, quality of teflon reflector, quality of coupling between sample and PMT, and sample directionality (if the source is in the "up" or "down" orientation). The decay time measurement for the reference measurement is shown in Figure 3.4. The decay time is a 3 component exponential decay, with a dominant decay time of 511 ns with a weight of 73%. Normally, the scintillation decay time is reported as a single exponential [1] due to the prominence of the fast component. However, the long components are an important consideration in this study, since the addition of codopants may affect the time and weight of scintillation decay components. Therefore, three-exponential fits are used to describe the scintillation decay for comparison between samples codoped with different species.

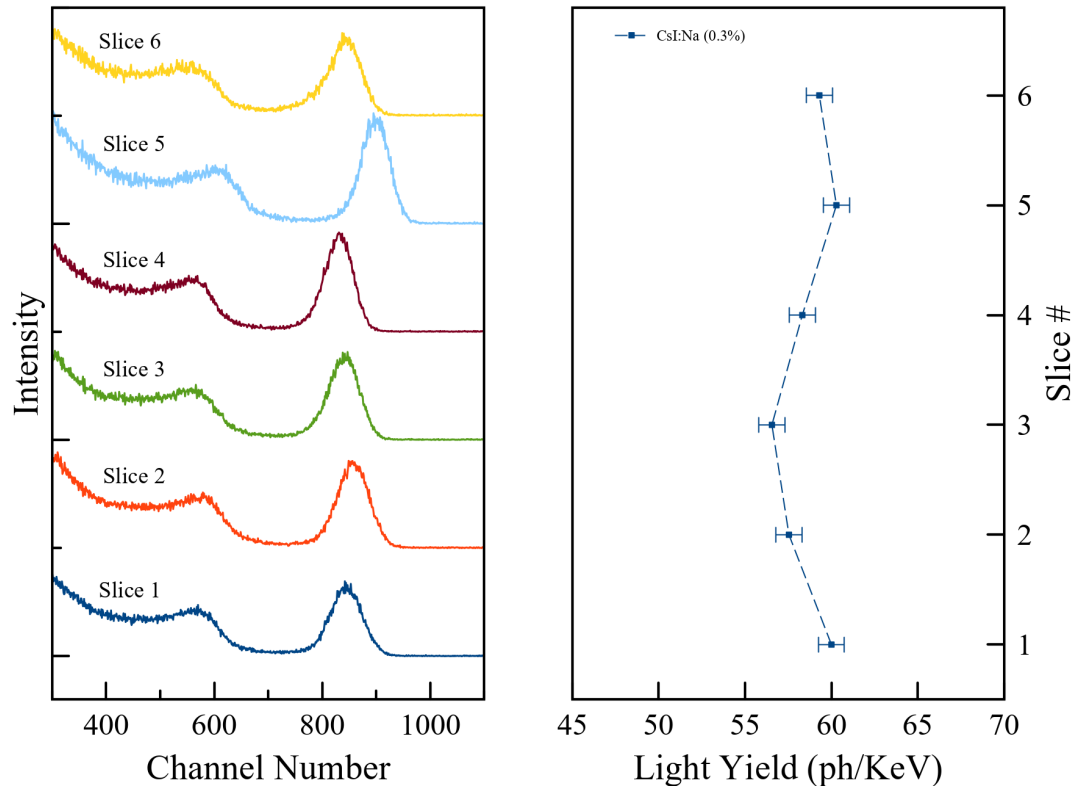


Figure 3.3: Light yield measurements and pulse height spectra of the CsI:Na reference.

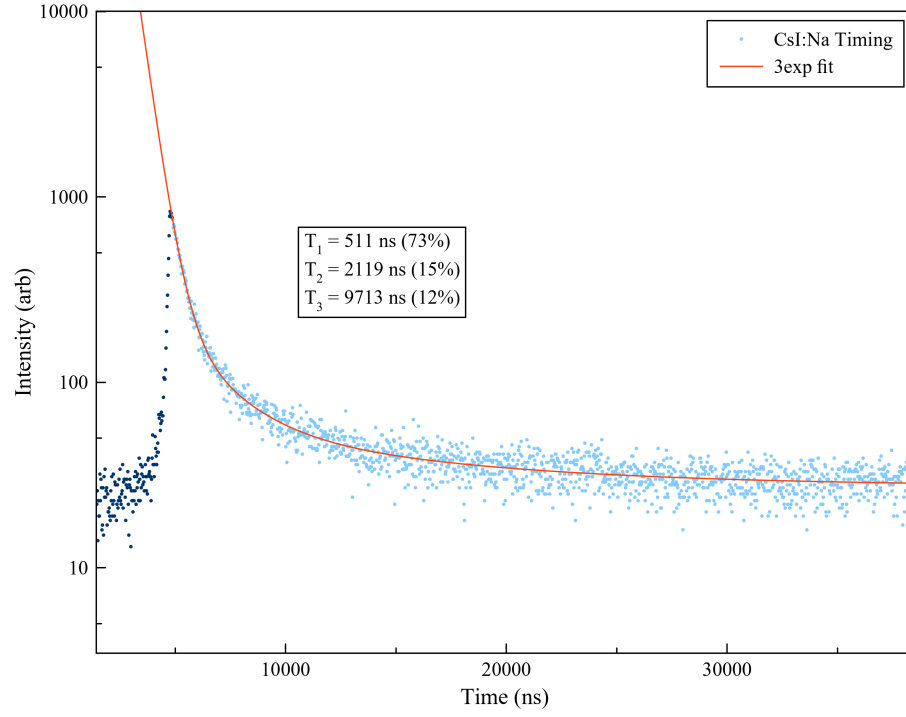


Figure 3.4: Scintillation decay measurement of CsI:Na reference crystal using $50 \mu\text{s}$ timing window.

3.2 CsI:Na,Eu Crystals

3.2.1 Crystal Growth and Quality

Three samples of codoped CsI:Na,Eu were grown, each with a different Eu concentration. The highest dopant concentration investigated was 0.5% Eu. The other codopant concentrations evaluated were 0.1% Eu and 0.01% Eu. Each Eu codoped crystal was grown together by the multi-crystal boat-growth via the Bridgman method in carbon coated ampoules. The crystals were translated at a rate of 2 mm per hour and cooled over a period of 48 hours. The crystals are shown in Figures 3.5, 3.6, 3.7. The 0.01% Eu crystal is colorless and clear throughout the entire boule, and each slab is of good optical quality. The 0.1% Eu crystal was colorless and clear before cutting into slabs. After cutting and polishing, yellow discolorations and inclusions were observed in the slabs close to the last-to-freeze section of the crystal. As seen in 3.6, the impurity rich section encompasses approximately 1/10th of the volume of the slab and is localized within a quadrant of the crystal. We believe that the impurity rich section is the result of a poor radial thermal gradient within the quartz holder that causes impurities to segregate to this region. The affects of the radial thermal gradient are pronounced in boat-growth of multiple ampoules; however, boat-growth was still chosen as the growth method of choice for screening a wide range of codopants. In this crystal, the impurities are assumed to be Eu^{2+} , and the yellow discoloration is the result of Eu^{2+} -localized cation vacancies. The 0.5% Eu crystal was observed to have intense internal stress, and is shown in Figure 3.7. Shown in Figures 3.8 and 3.9 are photos of crystals taken using polarized light, which allows for visualization of internal stresses. In Figure 3.8, we can see an image of a mostly stress-free crystal, which was an indication that the codopant was incorporated homogeneously and does not cause noticeable strain in the lattice. On the contrary, Figure 3.9 shows evidence of high stress near the defect-rich zone. A slice from the seed-end of the crystal (Slice 1) was free of any inclusions, and as a result, was relatively stress-free.

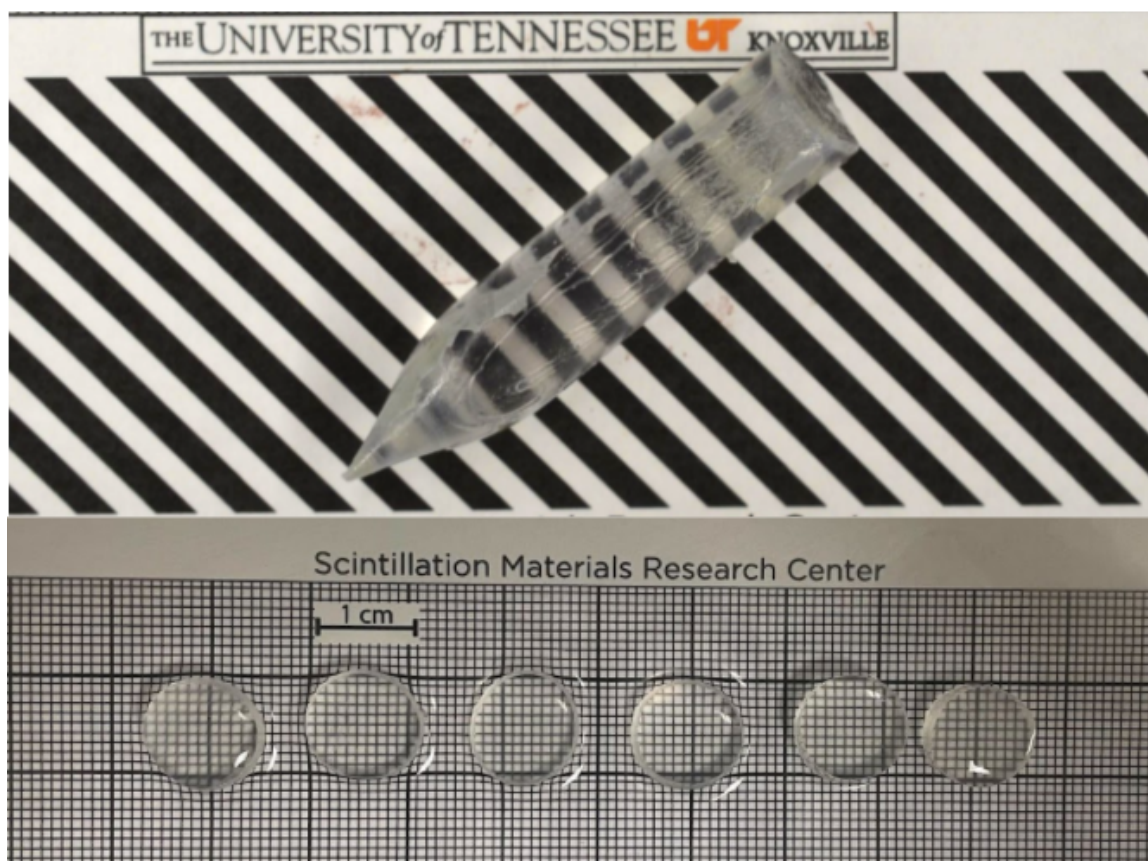


Figure 3.5: Top: CsI:Na,Eu(0.3,0.01%) crystal boule. Bottom: CsI:Na,Eu(0.3,0.01%) after boule was cut into six 4 mm slabs, with slabs ordered left to right in ascending order.

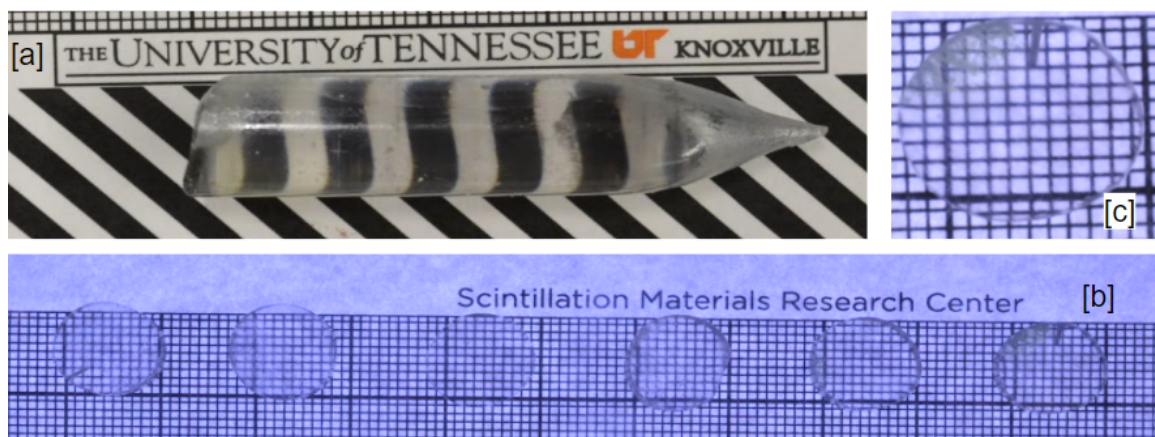


Figure 3.6: Top left: CsI:Na,Eu(0.3,0.1%) crystal boule. Top right: Slab containing yellow impurities and inclusions. Bottom: CsI:Na,Eu(0.3,0.1%) after boule was cut into six 4 mm slabs.

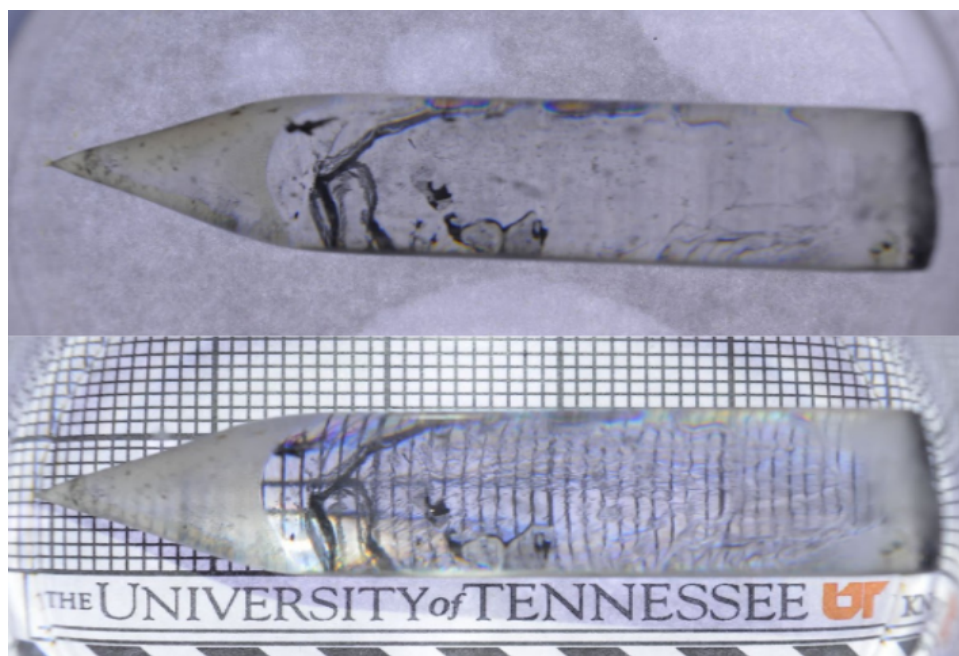


Figure 3.7: CsI:Na,Eu(0.3,0.5%) crystal boule. Note the extensive cracks and fissures along the boule.

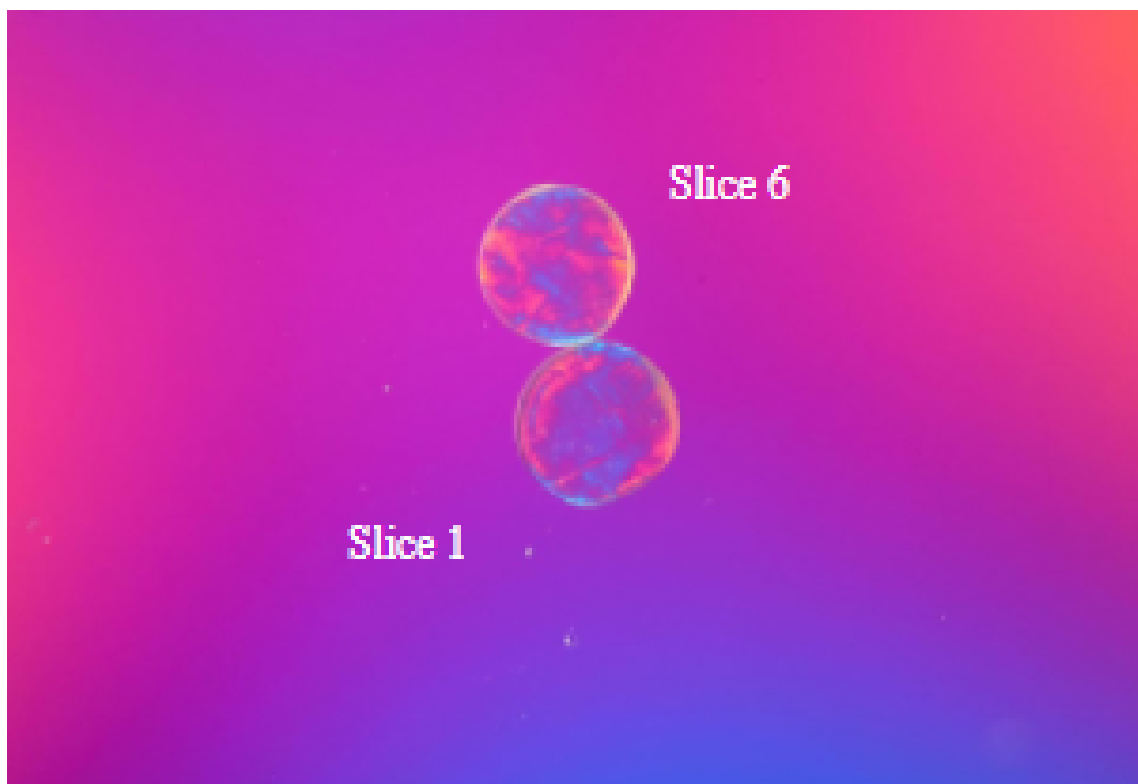


Figure 3.8: CsI:Na,Eu(0.3,0.01%) photographed using polarized light. Differences in color indicate stress within the crystal.

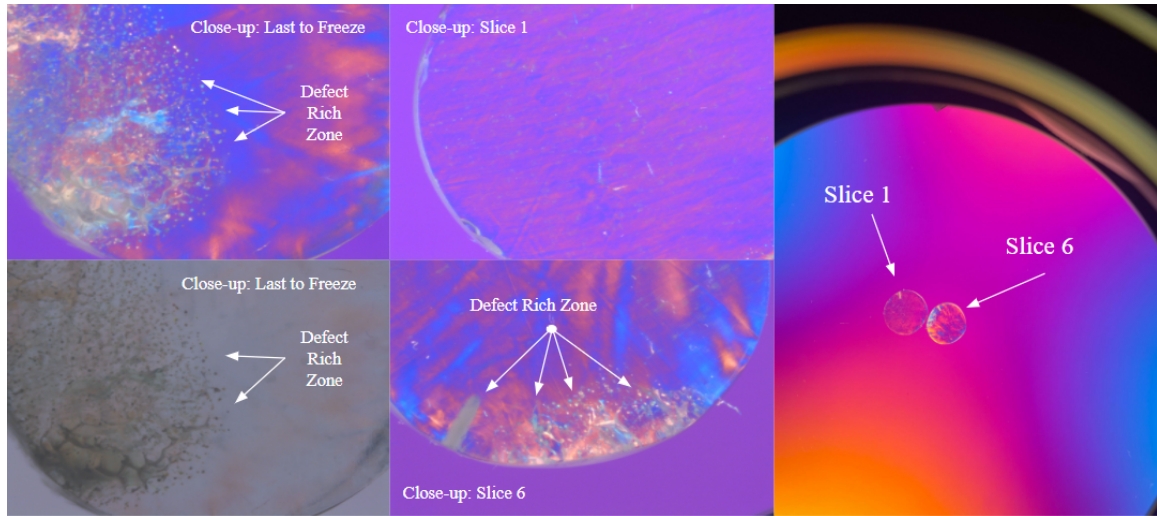


Figure 3.9: CsI:Na,Eu(0.3,0.1%) photographed using polarized light. Differences in color indicate stress within the crystal.

Higher quality crystals may be grown by individual single crystal growth via the Bridgman method where the crystal will be subject to a uniform radial thermal gradient.

3.2.2 Scintillation Properties of CsI:Na,Eu

The radioluminescence spectra for Eu codoped scintillators are shown below in Figure 3.12. The radioluminescence emission maximum was shown to have a redshift that was dependent on the Eu^{2+} concentration in the crystal.

Aside from the shifted radioluminescence maximum, the shape of the emission peak became markedly more narrow with [trend] dopant concentration, with the FWHM being minimized at a Eu concentration of 0.1%. The alteration of the radioluminescence spectra suggests a change in the scintillation process within CsI:Na, but more measurements are needed to determine the exact mechanisms at work.

The light yield for CsI:Na,Eu scintillators showed almost no difference between the light yield of non-codoped and Eu^{2+} scintillators, which suggested that there was direct competition between the old CsI:Na scintillation mechanism and the new scintillation mechanisms.

There are two proposed mechanisms that Eu may influence or directly control. The first proposed mechanism is Na serving as a scintillation sensitizer for Eu^{2+} . The Na localized STE relaxes and emits a photon that is within the excitation spectrum for Eu. The Eu ion absorbs the light produced by STE relaxation near the Na impurity and de-excites by releasing a photon with a longer wavelength. This process could explain the absence or decreased luminescent intensity from 350 nm to 400 nm that is intrinsic to CsI:Na scintillators, as the light in this region would be absorbed by the Eu ion and remitted at 450nm instead. If this is the new mechanism, one might expect to see a lengthened scintillation decay time that is a combination of the 600 ns decay time followed by the relaxation time of the Eu ion. The scintillation decay time measurements do not support this explanation.

The scintillation decay time measurements shown in Figure 3.14 instead suggest that there is a competing scintillation mechanism that has a long decay component. In CsI:Na,Eu(0.3,0.01%), the weight of the long component is increased by 20%, and the medium component by 20%. However, for CsI:Na,Eu(0.3,0.1%), the fast component is actually increased. This may be indicative of charge scavenging from the Eu^{2+} ions in the crystal.

The afterglow of CsI:Na,Eu scintillators was shown in Figure 3.15. The 0.1% crystal did not appear to have any meaningful of afterglow on the order of several seconds, but the 0.01% causes a significant decrease in afterglow. We do not know exactly why this is happening, but the result is remarkable.

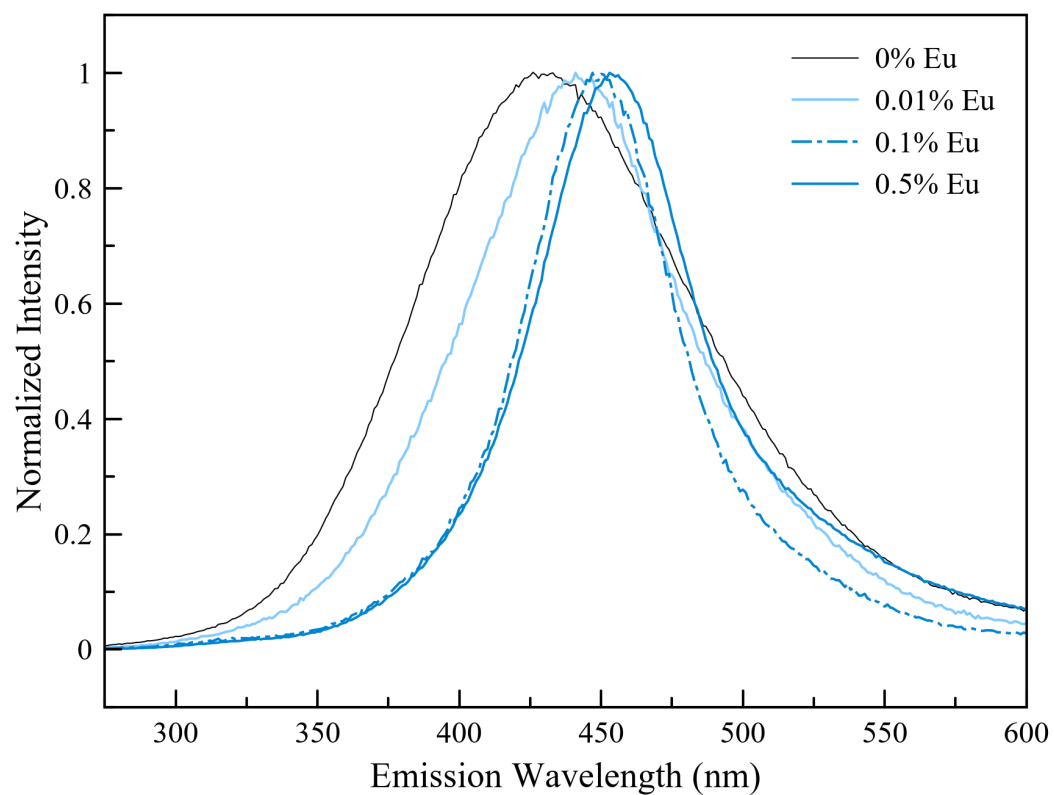


Figure 3.10: Radioluminescence spectra for CsI:Na,Eu scintillators. Na content for each sample is 0.3%

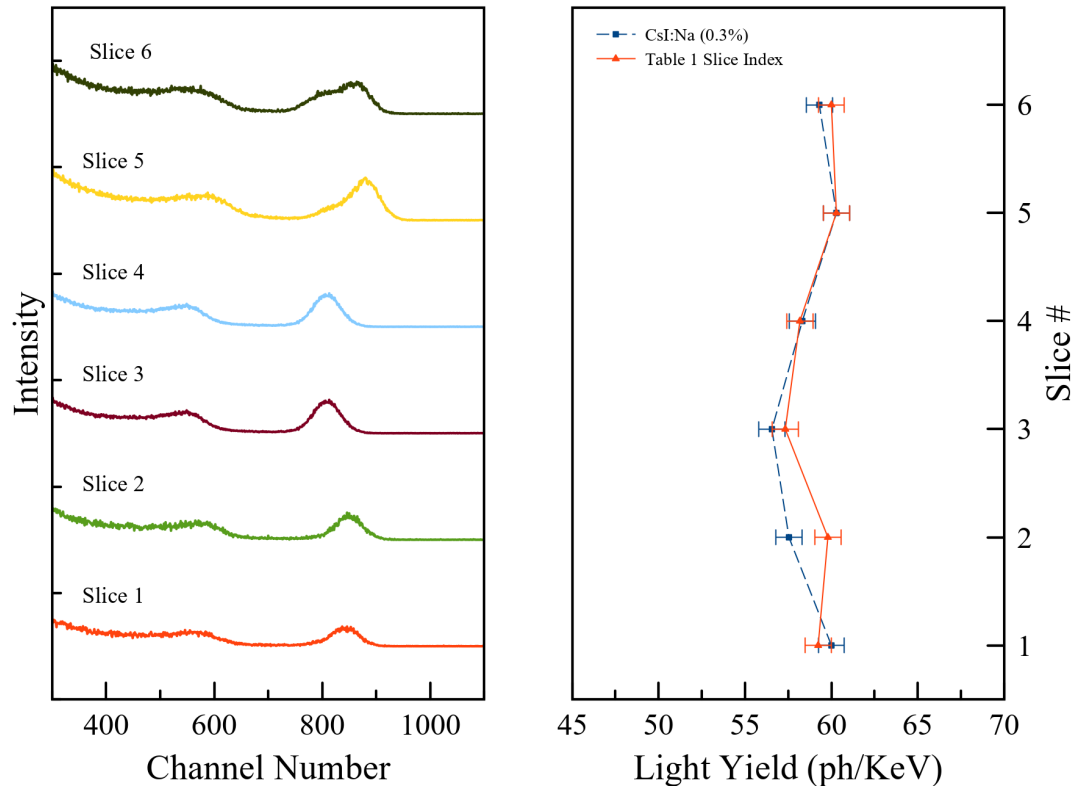


Figure 3.11: Pulse height spectra and light yield for CsI:Na,Eu(0.3,0.01%)

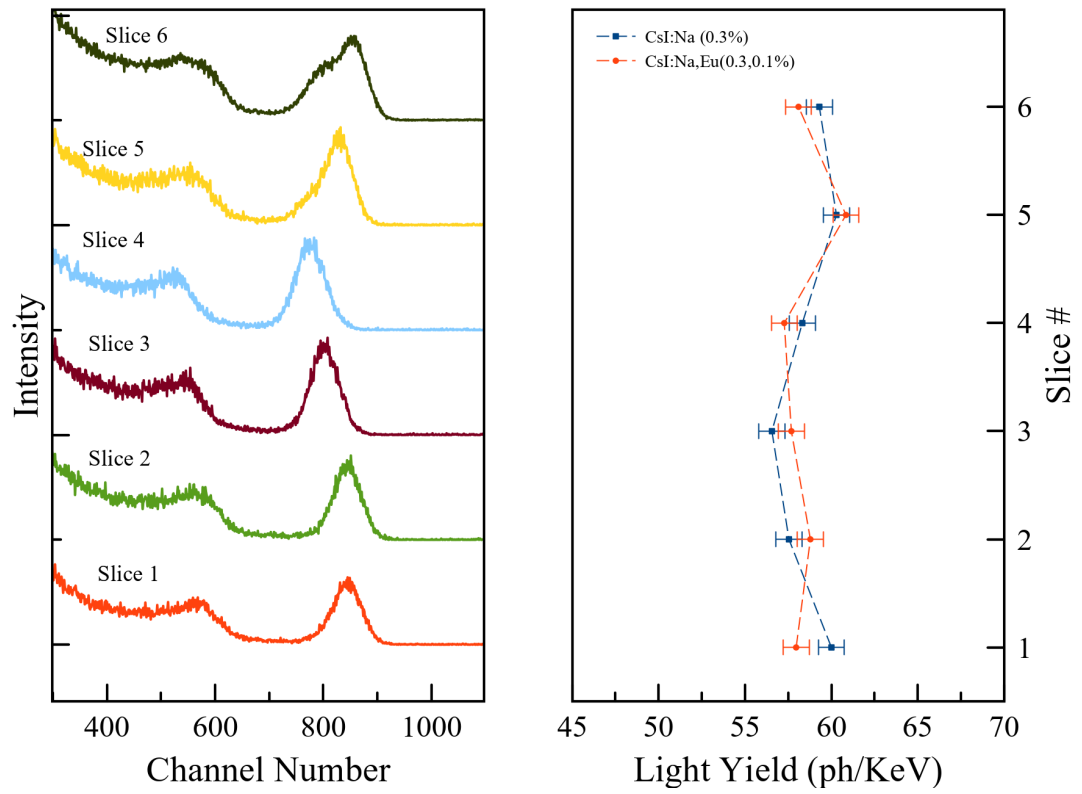


Figure 3.12: Pulse height spectra and light yield for CsI:Na,Eu(0.3, 0.1%)

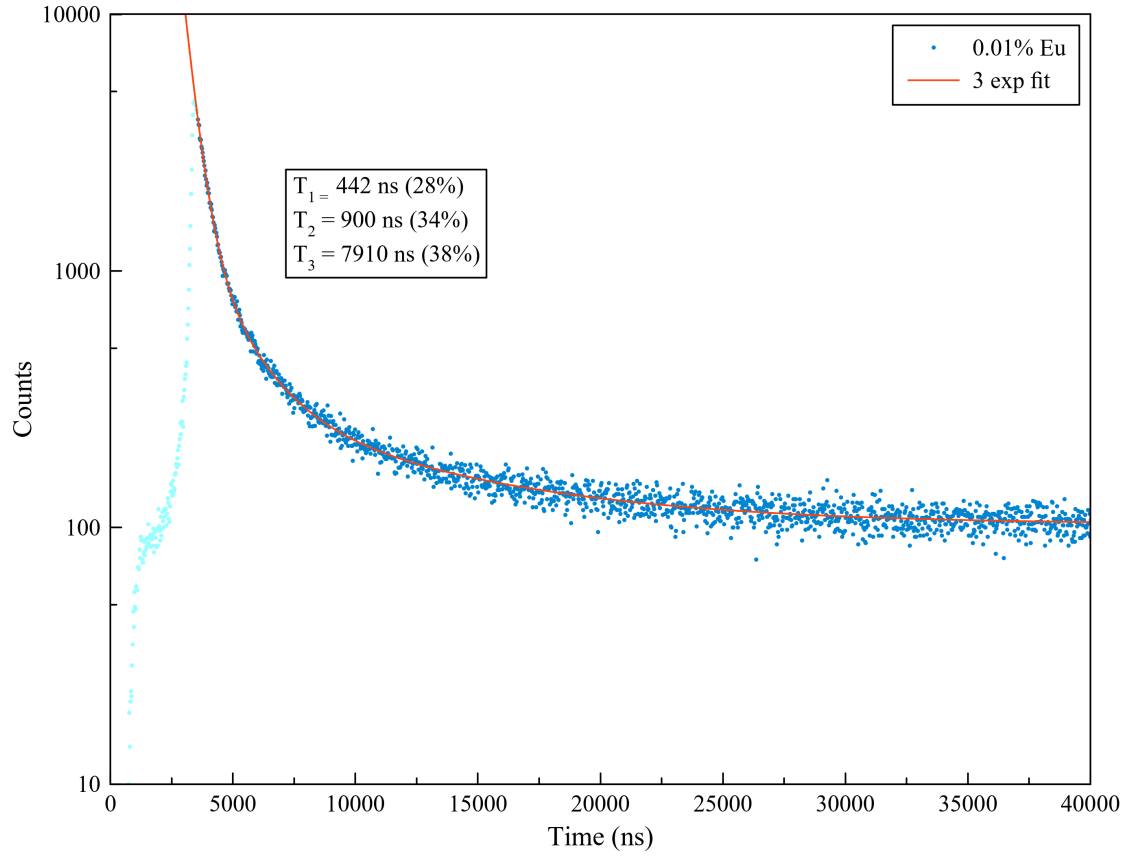


Figure 3.13: Scintillation decay times of CsI:Na,Eu(0.3,0.01%)

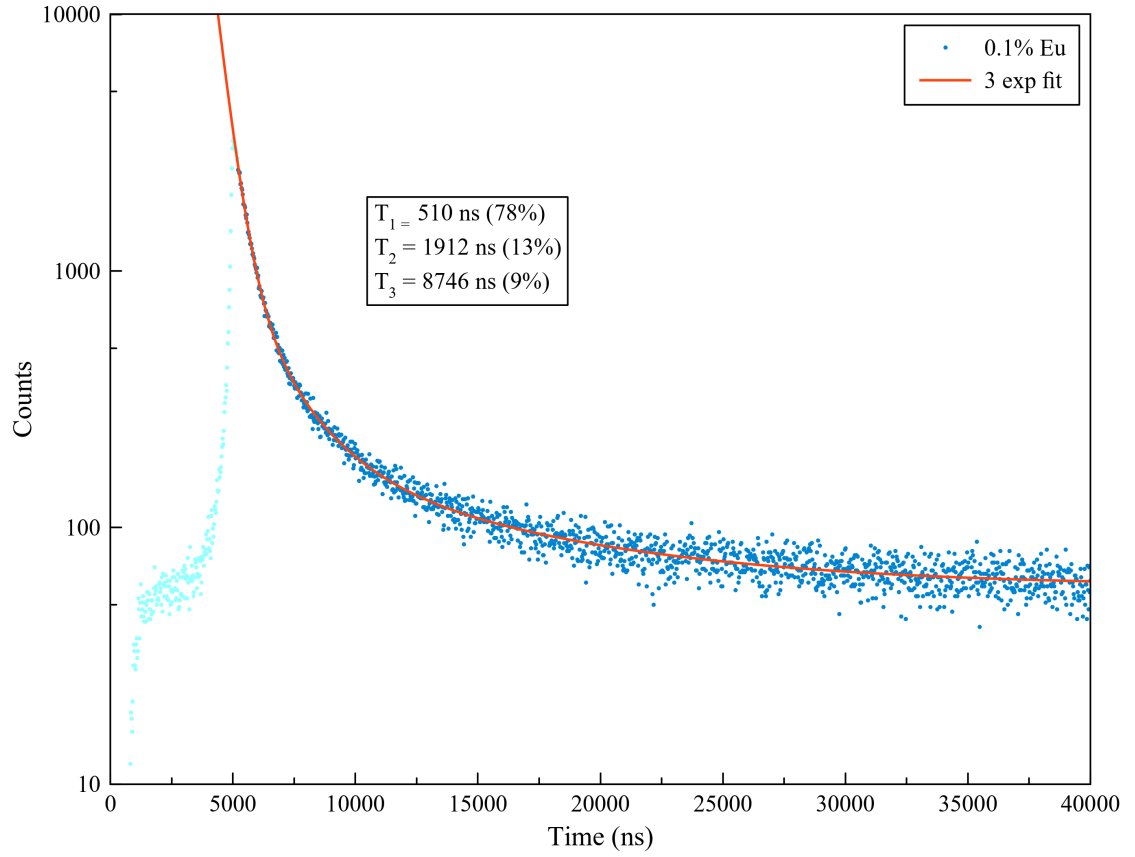


Figure 3.14: Scintillation decay times of CsI:Na,Eu(0.3, 0.1%)

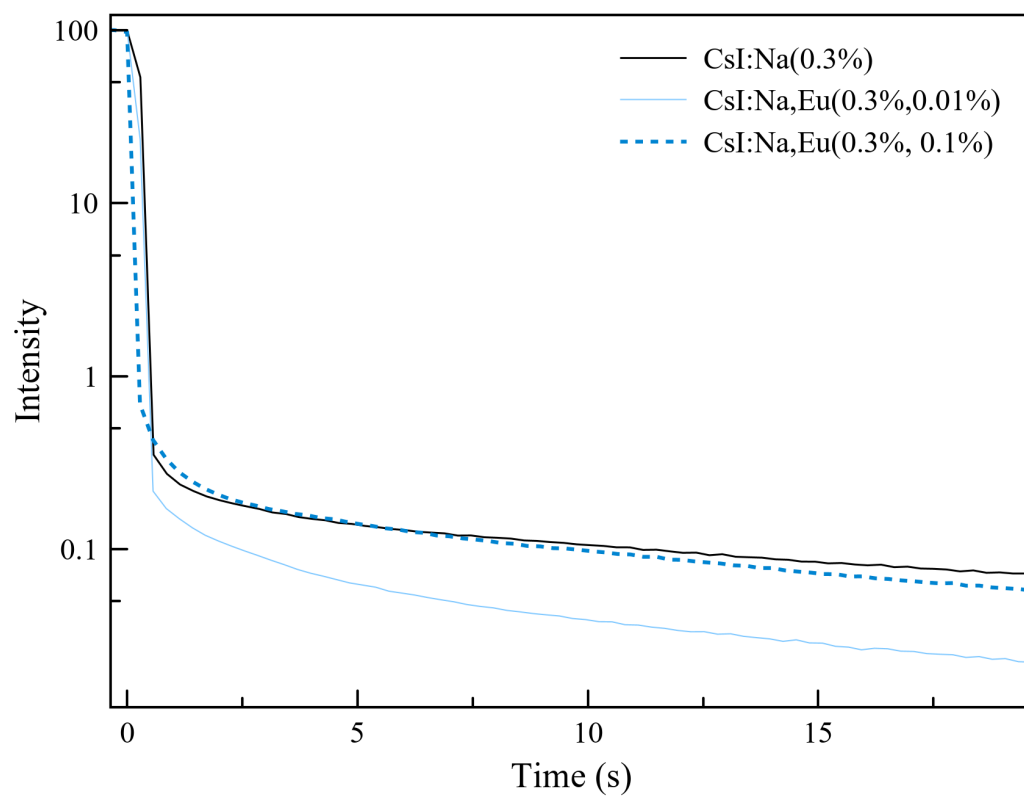


Figure 3.15: Afterglow of Eu codoped CsI:Na scintillators

3.3 CsI:Na,Yb Crystals

3.3.1 Crystal Growth and Quality

Two crystals of CsI:Na,Yb were grown; one with 0.1% Yb and another with 0.01% Yb. The crystals were grown via the Bridgman boat growth method, and were translated at a rate of 2 mm per hour. After growth, the crystals were cooled over a period of 48 hours.

The 0.1% Yb crystal was extracted from its carbon coated ampoule and a photograph was taken. This boule has a layer of yellow discoloration on the surface of the boule that could not be removed by gently cleaning the crystal. This yellow surface layer was able to be removed by gentle polishing of the outside with 600 grit sandpaper. The boule was then cut into 6 slabs and another picture was taken. Slices 1-4 are clear and have no noticeable impurities, but slices 5 and 6 have relatively large opaque regions with visible inclusions. These inclusions are similar to those found in the 0.1% Eu crystal, and the explanation for the discoloration is the formation of cation vacancies that compensate for a high concentration of Yb^{2+} ions in the lattice. The radioluminescence spectra of the Yb codoped scintillators presents another case of a red shifted radioluminescence spectra. For the heavily Yb doped sample, there is a 50 nm red shift in the radioluminescence spectra, while for the lightly Yb doped sample there is nearly no change in the radioluminescence spectra. Photoluminescence shows two excitation peaks appearing at 360 nm and 410 nm, which are well within the emission wavelengths for CsI:Na. When excited by either of these wavelengths, the crystal emits at 3 primary wavelengths: 455 nm, 475 nm, and 585 nm.

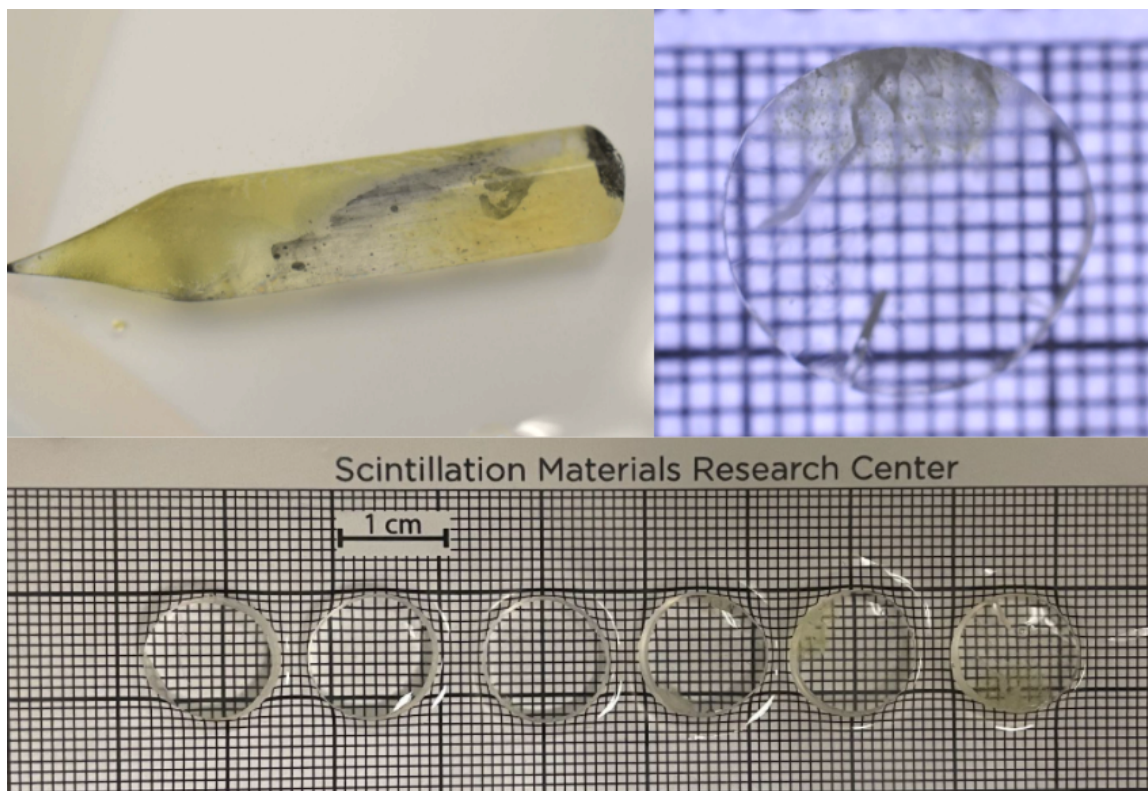


Figure 3.16: CsI:Na,Yb(0.3,0.1)% Crystal qualities. Top left: crystal after extraction from ampoule. Bottom: Slabs cut from the main boule in ascending order from left to right. Top right: Image of slice 6, the slice with the most visible inclusions and impurities.

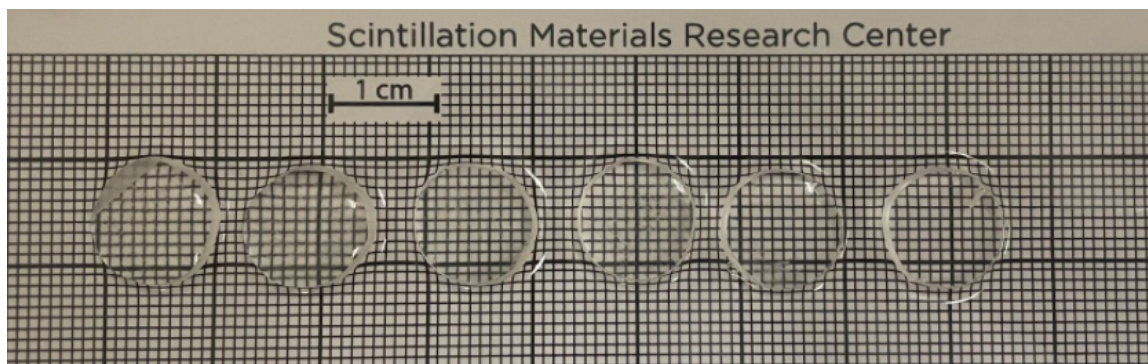


Figure 3.17: CsI:Na,Yb(0.3,0.01)% crystal slabs. All slabs are transparent and clean, with the exception of two cutting artifacts located on slabs 1 and 6.

3.3.2 Scintillation Characteristics of CsI:Na,Yb

The two peaks located around 455 and 475 nm are indicative of Yb in the 2+ charge state, however, the cause of broader emission at 560nm is unknown. These emission bands in that are present in both Yb codoped samples are dwarfed by the Na emission at 420 in photoluminescence, but the radioluminescence for the heavily Yb codoped samples shows a strong emission at 475 nm. There is no evidence of the 585nm emission in the radioluminescence, and attempts to make measurements on this emission have had null results.

It is apparent that the scintillation mechanism in CsI:Na,Yb scintillators is different from CsI:Na scintillators. The same explanations for Eu codoped scintillators may be true for these compositions as well. The sensitization mechanism is physically possible, as the excitation bands for Yb lie within the emission of CsI:Na. The direct stimulation of Yb ions is also possible, and a sample of CsI:Yb can be analyzed in order to evaluate the contributions from this mechanism. The light yield data for Yb shows a significant increase to the light yield of CsI:Na scintillators. The light yield for CsI:Na,Yb crystals is consistently above the light yield for CsI:Na crystals except for select samples with severe dopant segregation and therefore areas with opaque impurities.

The timing characteristics of CsI:Na,Yb scintillators are shown in figures 3.22 and 3.23. Interestingly, the 0.01% Yb sample has a faster scintillation decay component than all of the other scintillation measurements, and reduce the other scintillation decay components by about 30 - 40%. The 0.1% Yb crystal has a similar effect to Eu codoped scintillators in that it increases the percentage of the longer components while reducing the effect of the shorter components.

The afterglow data for CsI:Na,Yb is presented in Figure 3.23. Remarkably, both concentrations of Yb in CsI:Na reduce the afterglow by close to an order of magnitude. Following the trend from Eu codoped CsI:Na, the lower concentration of Yb has a substantially lower afterglow than the higher Yb concentration crystal.

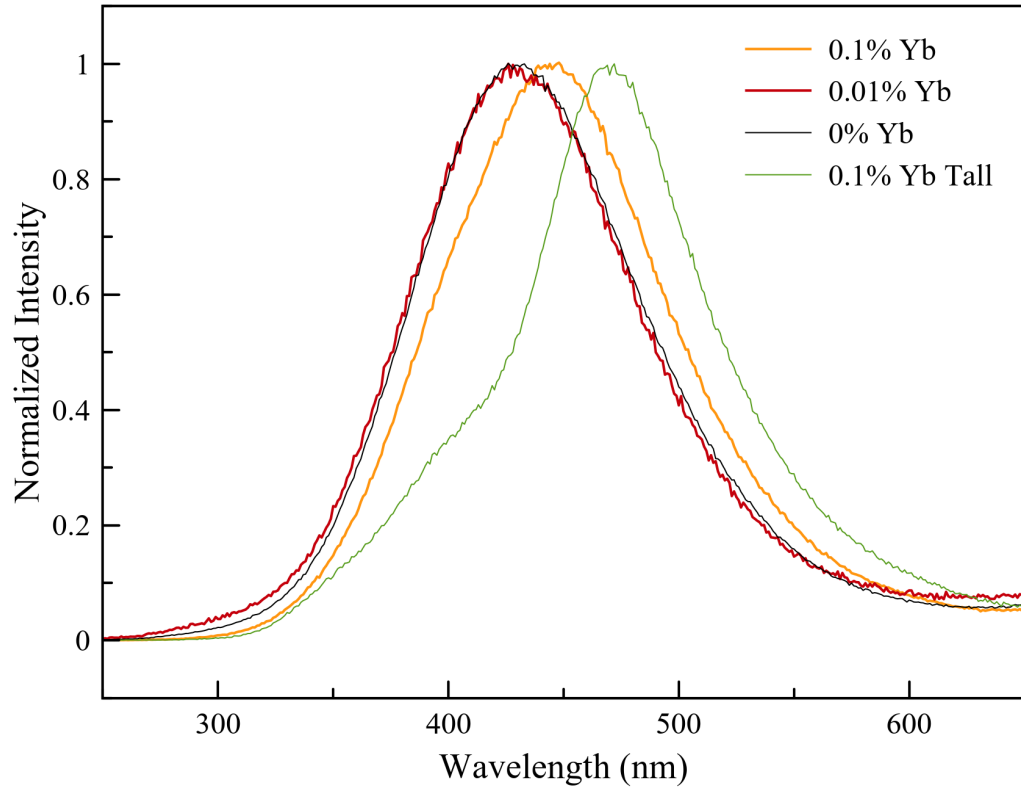


Figure 3.18: Radioluminescence spectra for CsI:Na,Yb scintillators. Na content for each sample is 0.3%. The Yb tall measurement was carried out with a 12mm tall boule, and shows the effect of Yb-induced self absorption on the radioluminescence spectra.

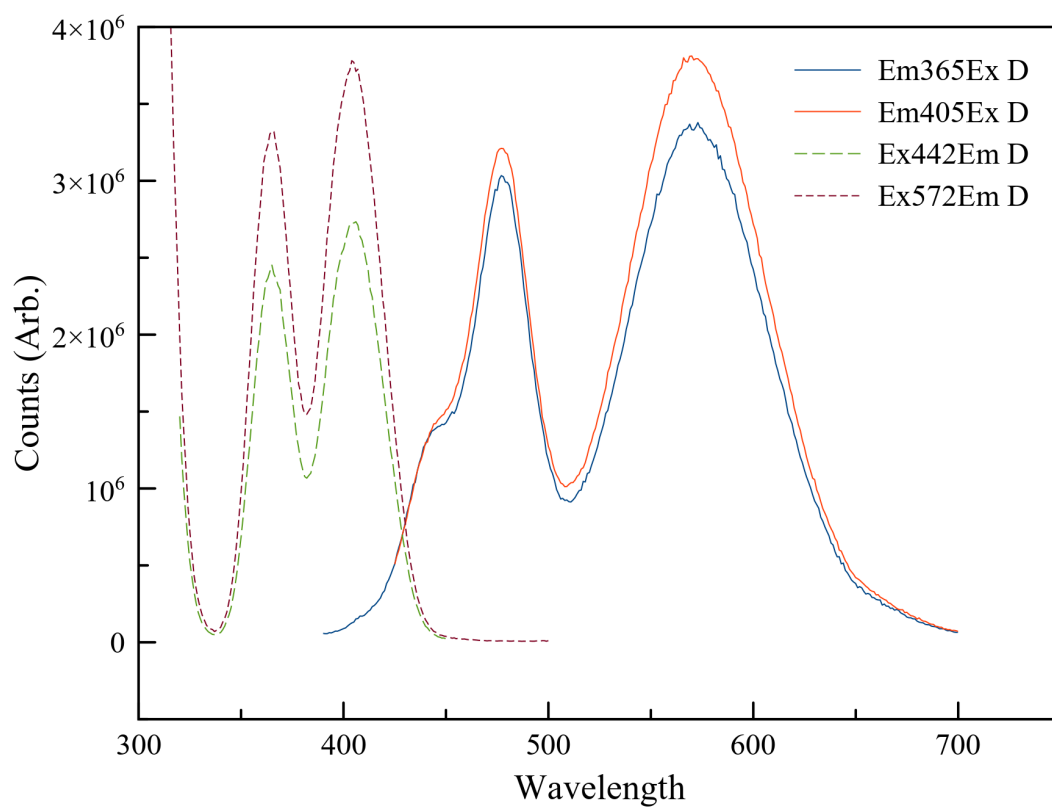


Figure 3.19: Photoluminescence excitation / emission spectra for CsI:Na,Yb(0.3,0.1%) scintillators.

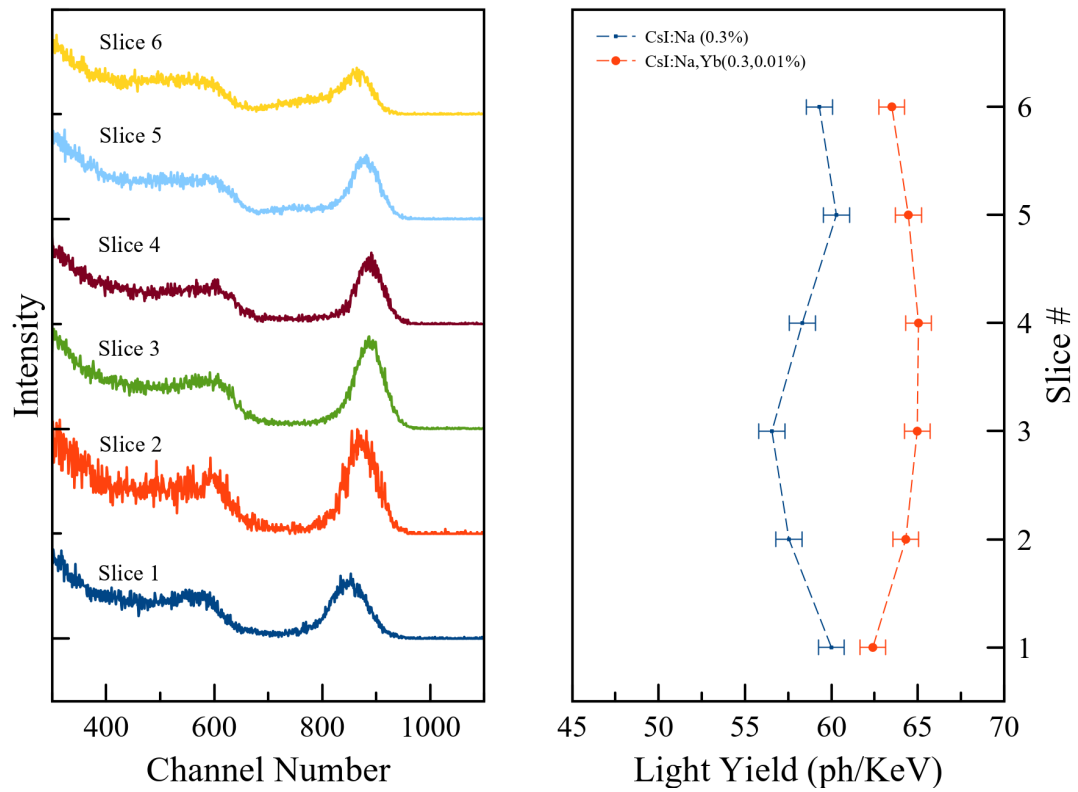


Figure 3.20: Light yield and pulse height spectra of CsI:Na,Yb(0.3,0.01%) slabs

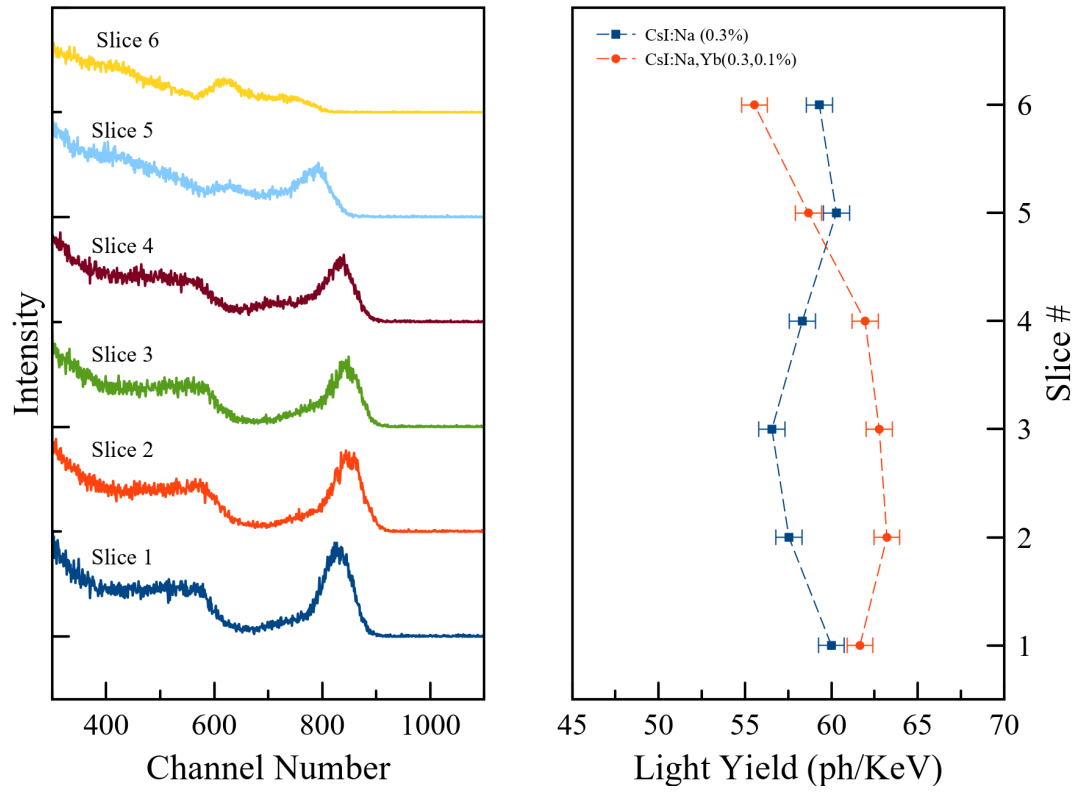


Figure 3.21: Light yield and pulse height spectra of CsI:Na,Yb(0.3,0.1%) slabs

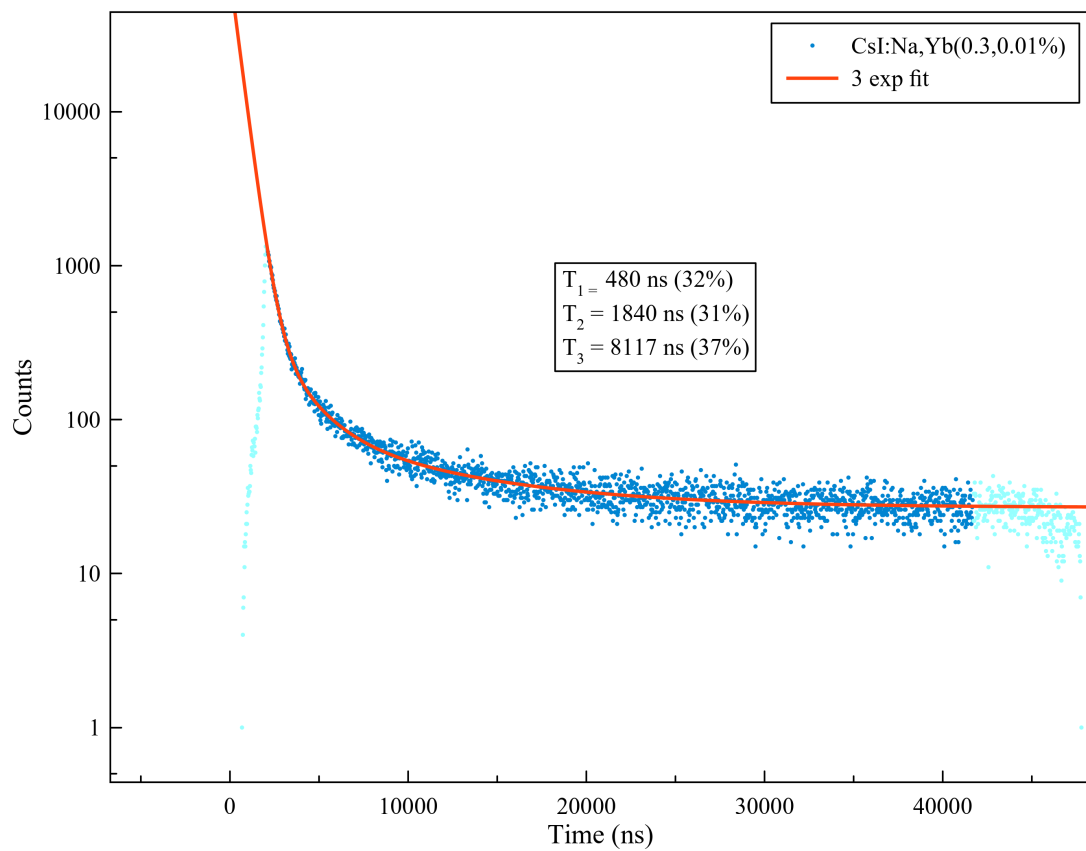


Figure 3.22: Scintillation decay time of CsI:Na,Yb(0.3,0.01%)

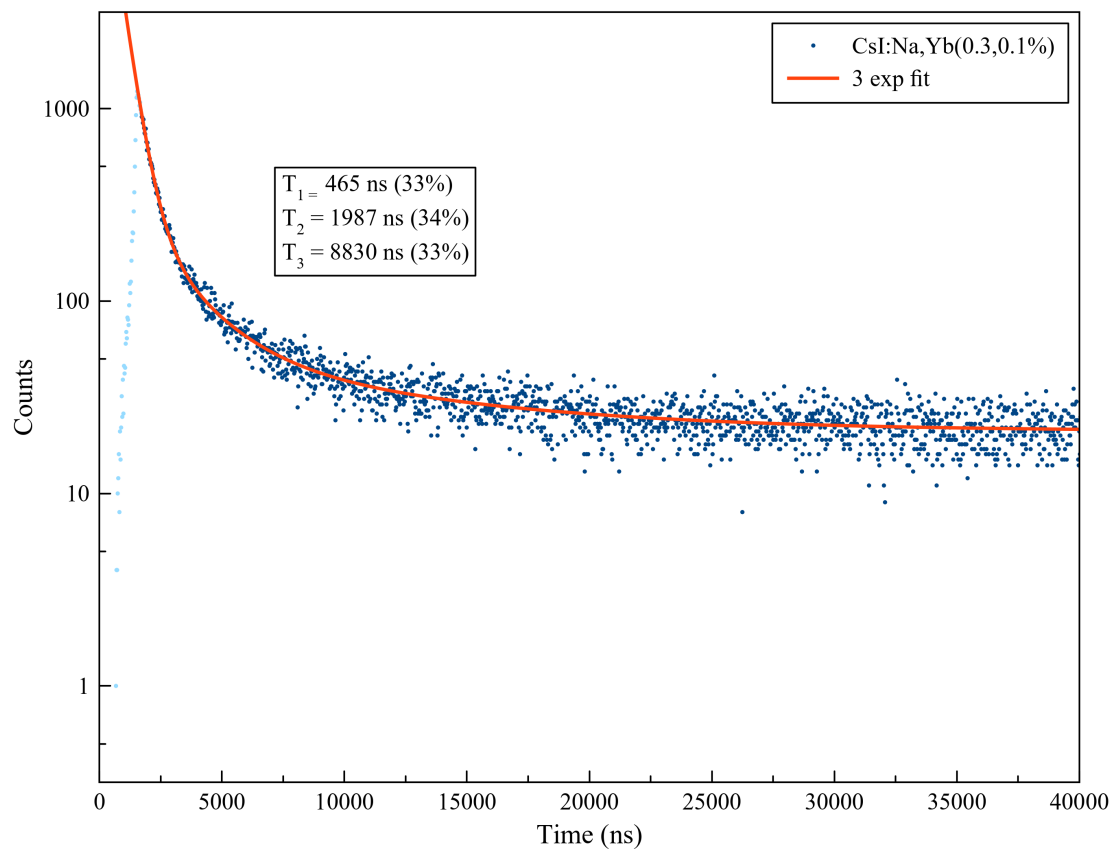


Figure 3.23: Scintillation decay time of CsI:Na,Yb(0.3,0.1%)

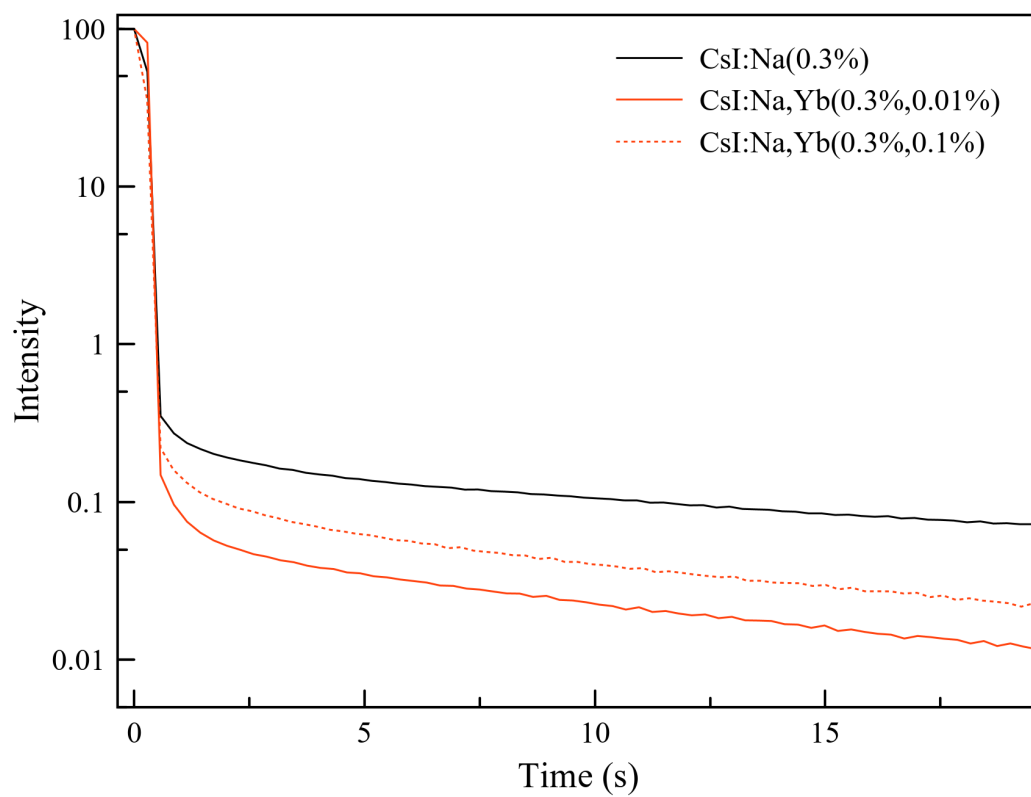


Figure 3.24: Afterglow of Yb codoped CsI:Na scintillators

3.4 CsI:Na,Sm Crystals

3.4.1 Crystal Growth and Quality

Two crystals were grown for the codoping study, one crystal with a codopant concentration of 0.1%. The resulting crystals are shown in Figures 3.25 and 3.26. The crystals are both colored a rich teal green, but with varying intensities as a function of Sm concentration. The color does not appear to be uniform across the slabs, with the outside edges being more colored than the center of the boule. The non-uniformity of the samples is very apparent in Figure 3.25, and to a lesser degree in Figure 3.26.

3.4.2 Scintillation Characteristics of CsI:Na,Sm

Sm was selected as a codopant with the sensitization mechanism in mind. In theory, the CsI:Na scintillation light should be absorbed by Sm ions, and the Sm ions would release the energy in the form of red or infrared light that would be better suited to red-sensitive photo detectors. The radioluminescence spectra of CsI:Na,Sm scintillators are presented in Figure 3.32. There is no observable change in radioluminescence spectra for CsI:Na,Sm(0.3,0.01%), but a noticeable shift in the radioluminescence peak wavelength for CsI:Na,Sm(0.3,0.1%). The light yield of CsI:Na,Sm are presented in Figure 3.28 and 3.29. The light yield of Sm codoped CsI:Na is drastically reduced as a function of Sm in the crystal. An explanation of the decrease in light yield could be the lack of transparency of the samples to the blue light that CsI:Na emits, but absorbance and transmittance measurements are required to make a definitive determination on whether this is the true cause of light yield reduction. Sm codoping resulted in an increase of the weight of slower decay components, though the scintillation decay components were all shortened compared to the CsI:Na reference. The afterglow was reduced in CsI:Na,Sm by an order of magnitude compared to the CsI:Na reference.

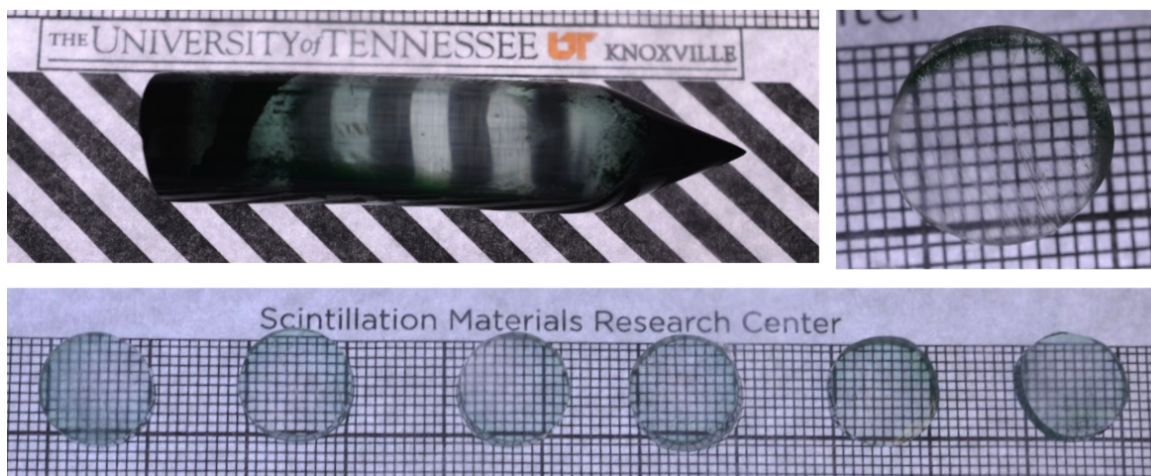


Figure 3.25: CsI:Na,Sm(0.3,0.1)% Crystal qualities. Top left: crystal after extraction from ampoule. Bottom: Slabs cut from the main boule in ascending order from left to right. Top right: Image of slice 6, the slice with the most visible inclusions and impurities.



Figure 3.26: CsI:Na,Sm(0.3,0.01)% Crystal qualities. Top left: crystal after extraction from ampoule. Bottom: Slabs cut from the main boule in ascending order from left to right. Top right: Image of slice 6, the slice with the most visible inclusions and impurities.

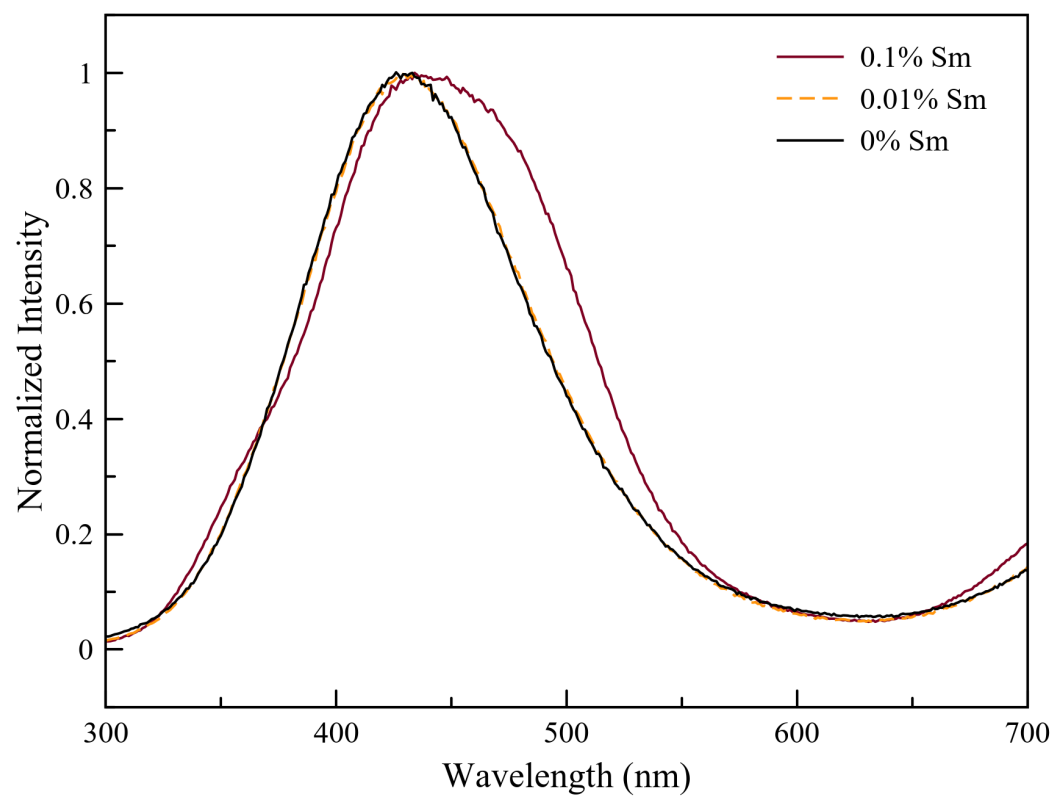


Figure 3.27: CsI:Na,Sm radioluminescence spectra compared to reference CsI:Na.

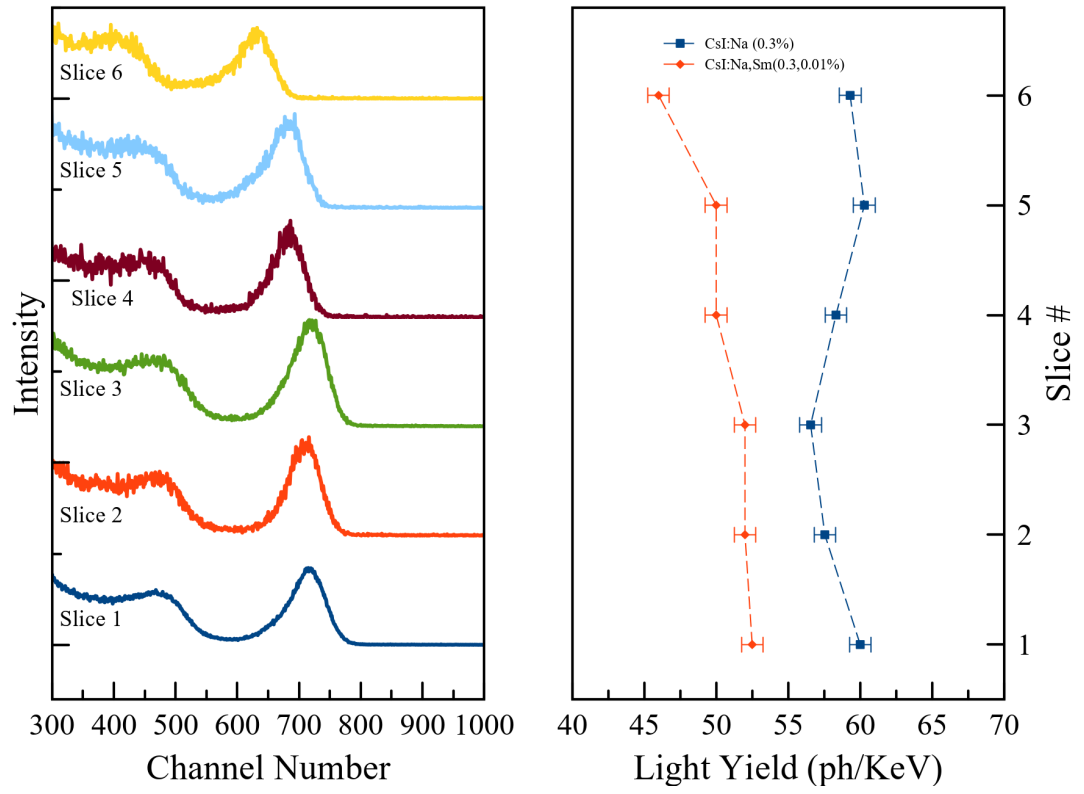


Figure 3.28: Light yield and pulse height spectra of CsI:Na,Sm(0.3,0.01%) slabs

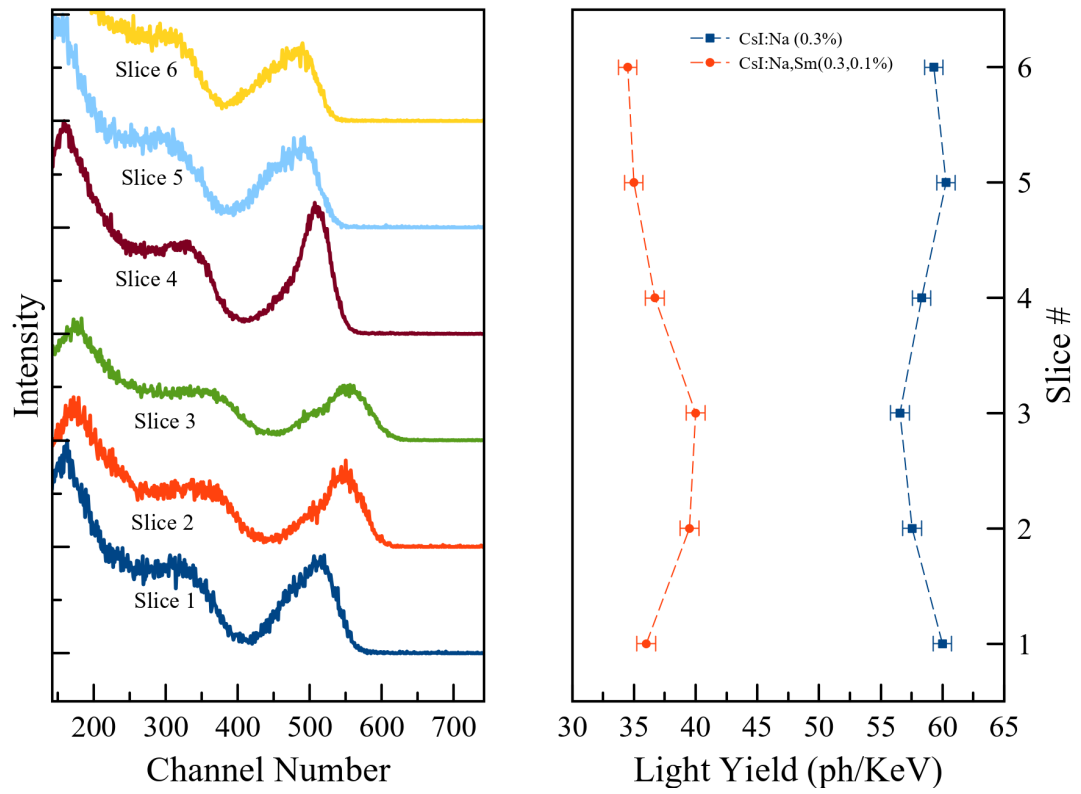


Figure 3.29: Light yield and pulse height spectra of CsI:Na,Sm(0.3,0.1%) slabs

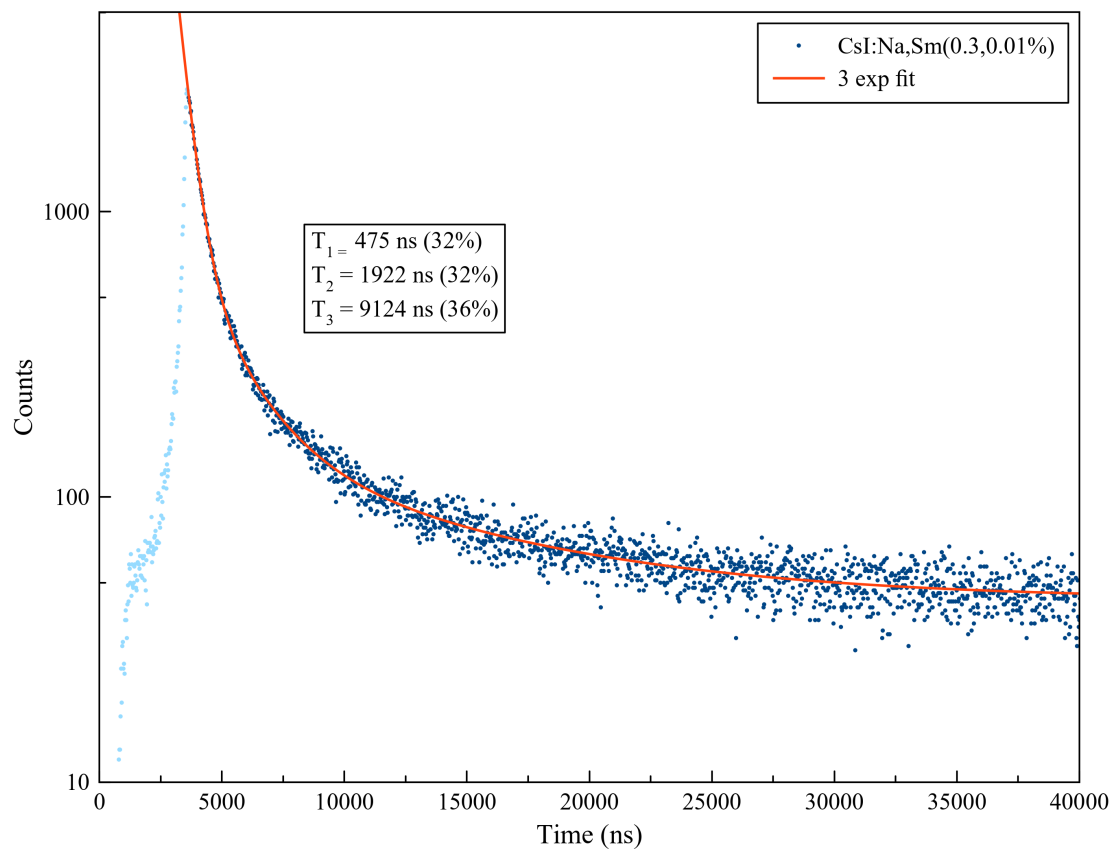


Figure 3.30: Scintillation decay times of CsI:Na,Sm(0.3,0.01%) slabs

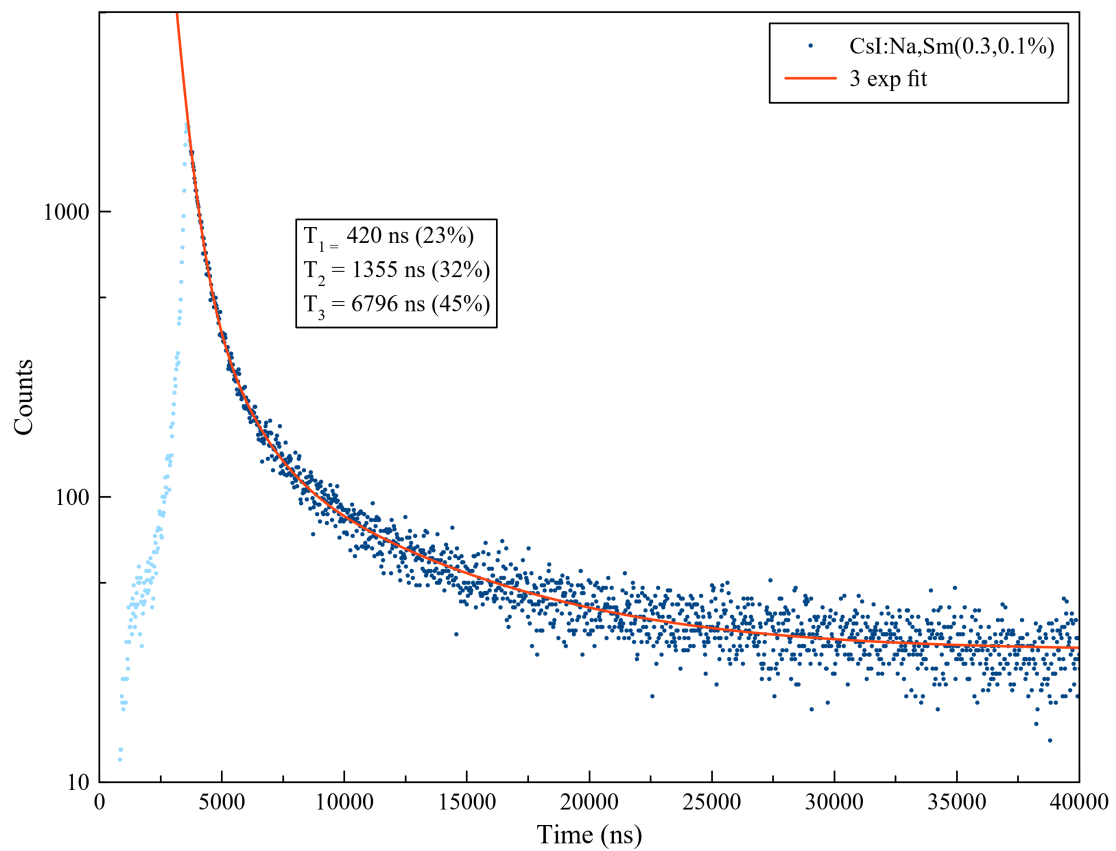


Figure 3.31: Scintillation decay times of CsI:Na,Sm(0.3,0.1%) slabs

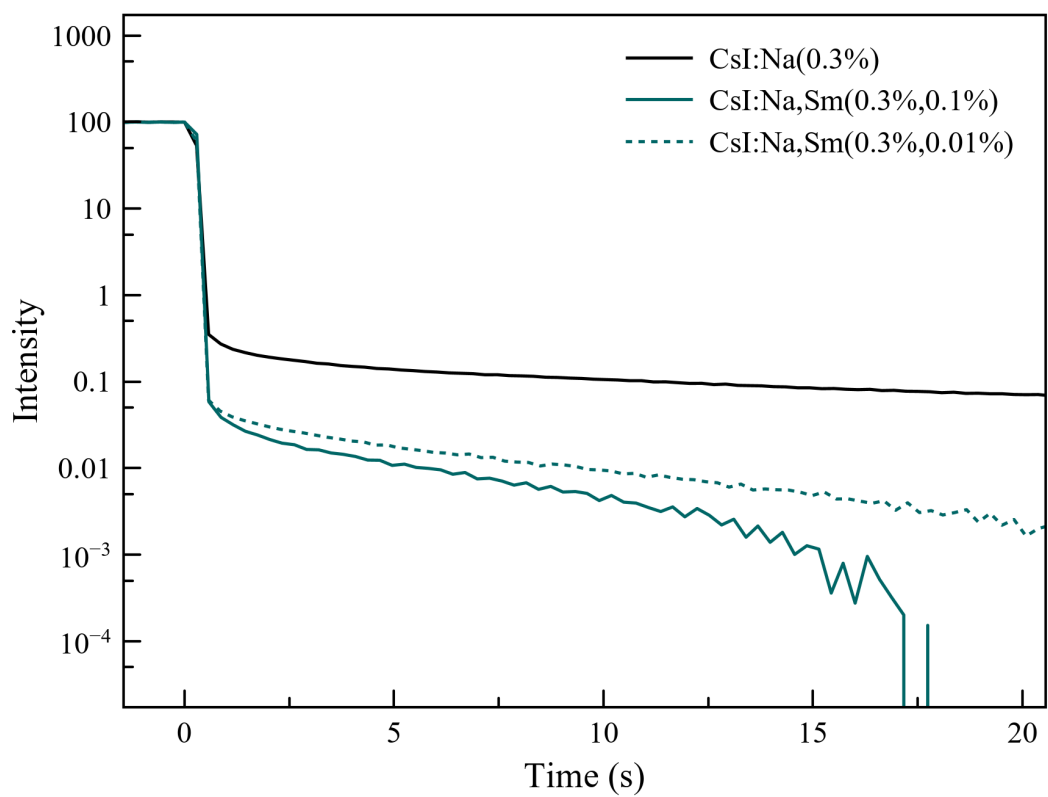


Figure 3.32: Afterglow of CsI:Na,Sm samples

3.5 CsI:Na,Ca Crystals

3.5.1 Crystal Growth and Quality

Two crystals were grown for the codoping study, one crystal with a codopant concentration of 0.3% Ca and another of 0.01% Ca concentration. Both CsI:Na,Ca crystals were grown by themselves in a Bridgman furnace. Each crystal was grown at a rate of 3 mm per hour, and cooled over a period of 24 hours. Upon removal from the ampoule, it was found that the 0.3% Ca crystal was heavily cracked and could not be processed like the other samples. Only two samples were obtained from the 0.3% Ca boule, as the rest of the crystal either shattered into small pieces upon cutting or disintegrated when polishing. The 0.01% Ca Codoped sample was very similar in quality to the other CsI:Na crystals grown, and intact slices were obtained. Despite being easy to cut into slabs, the 0.01% Ca crystal was very easy to injure during polishing. While polishing, both samples had 0.5 mm diameter pieces of crystal cleave off of the stock and scratch the surface of the sample. This made polishing difficult in comparison to the other codoped samples, but was mitigated by polishing with a light grit sandpaper for a longer duration of time.

3.5.2 Scintillation Characteristics of CsI:Na,Ca

The radioluminescence spectra of CsI:Na,Ca crystals does not show any difference from standard CsI:Na crystals. The light yield of CsI:Na,Ca scintillators is similar to the light yield of CsI:Na,Yb scintillators. Like the Yb codoped scintillators, the light yield is increased by 8%. Despite not displaying any obvious changes in the luminescence mechanism, the light yield has improved which is very interesting. This implies that there is another scintillation mechanism that remains unaccounted for. A clue for what this scintillation mechanism may be can be found in the analysis of the ionic size of both Ca and Yb ions. With coordination number of VI, Ca has an ionic radius of 1.00 Å, and Yb has an ionic radius of 1.02 Å. These ionic radii are

very similar, and could have something to do with the increased light yield that has been observed.

Another interesting characteristic of CsI:Na,Ca scintillators is the scintillation decay time. The scintillation decay time for this compound was found to have two primary components: a primary component of 1.2 microseconds and a secondary component of 9.3 microseconds, compared to the standard decay components of 0.54 microseconds and 2.8 microseconds. The afterglow of CsI:Na,Ca(0.3,0.01%) is shown in figure [3.38](#). The afterglow is improved by approximately a factor of five.

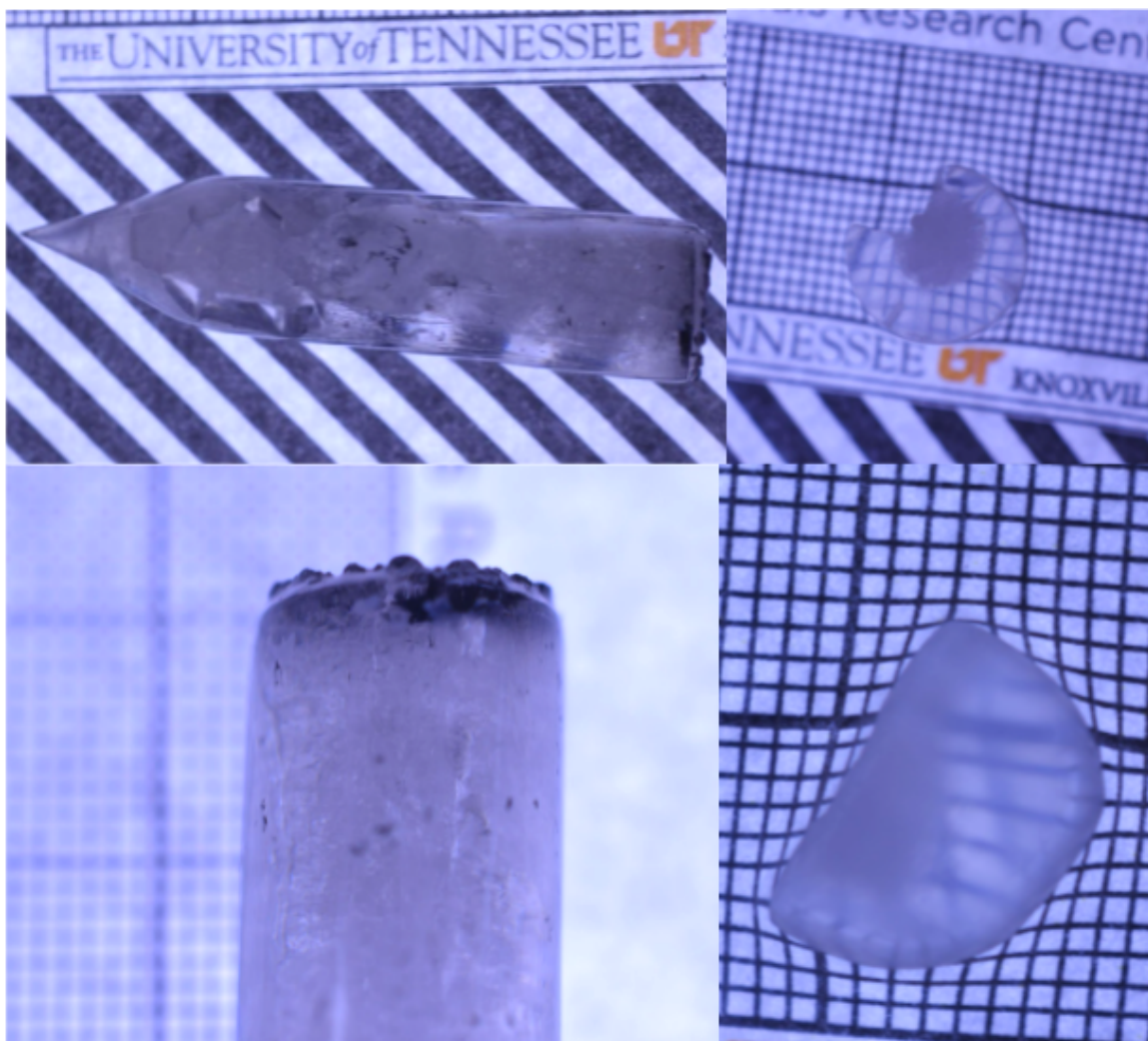


Figure 3.33: CsI:Na,Ca(0.3,0.3)% Crystal qualities. Top left: crystal after extraction from ampoule. Bottom Left: Close up of boule before cutting. Top right: Cut and polished intact cylinder with visible coring. Bottom right: Second largest surviving piece after cutting also shows evidence of coring.

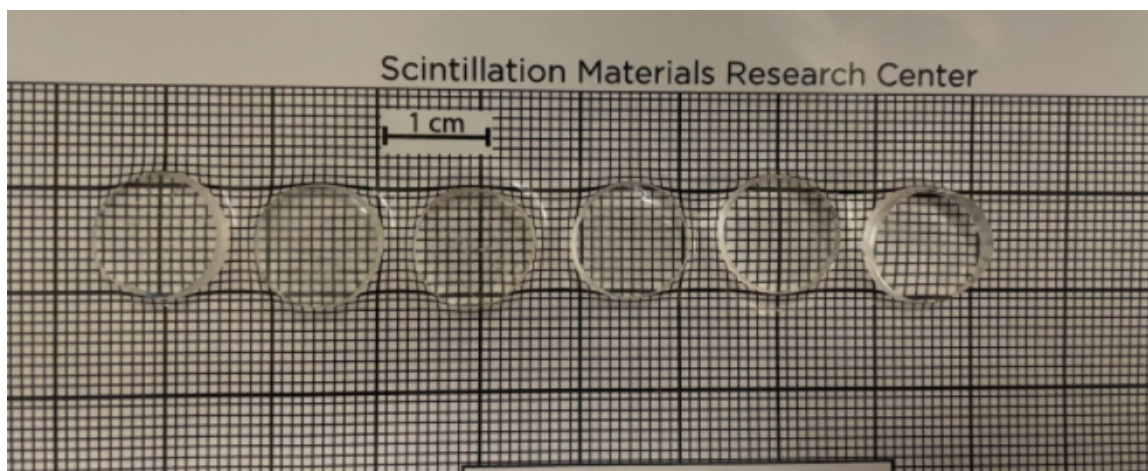


Figure 3.34: CsI:Na,Ca(0.3,0.01)% slabs cut from the boule with slices ordered left to right in ascending order

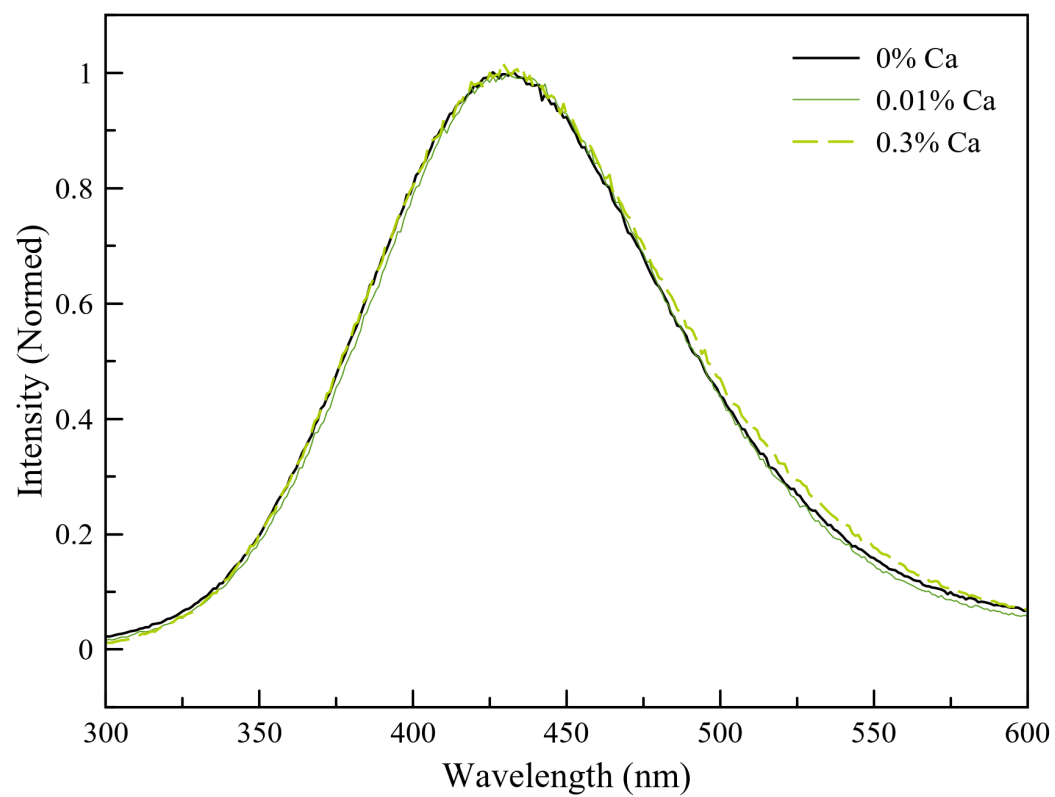


Figure 3.35: CsI:Na,Ca(0.3,0.01)% radioluminescence spectra.

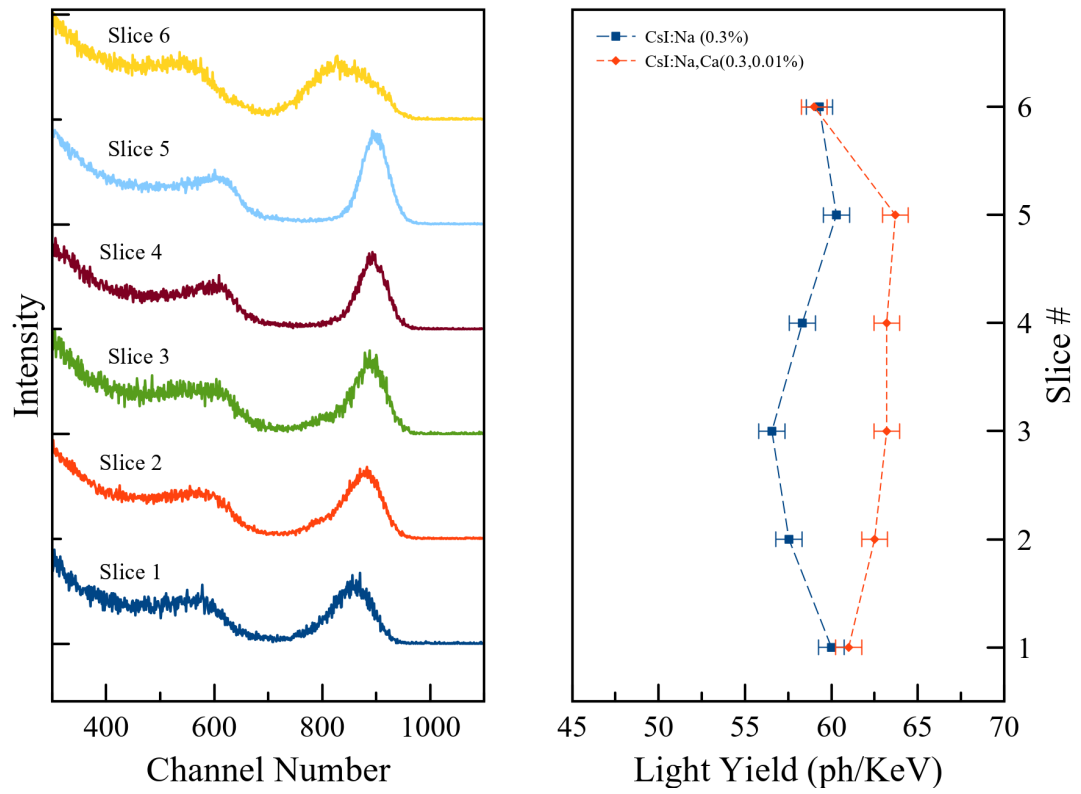


Figure 3.36: Light yield and pulse height spectra of CsI:Na,Ca(0.3,0.01)% slabs.

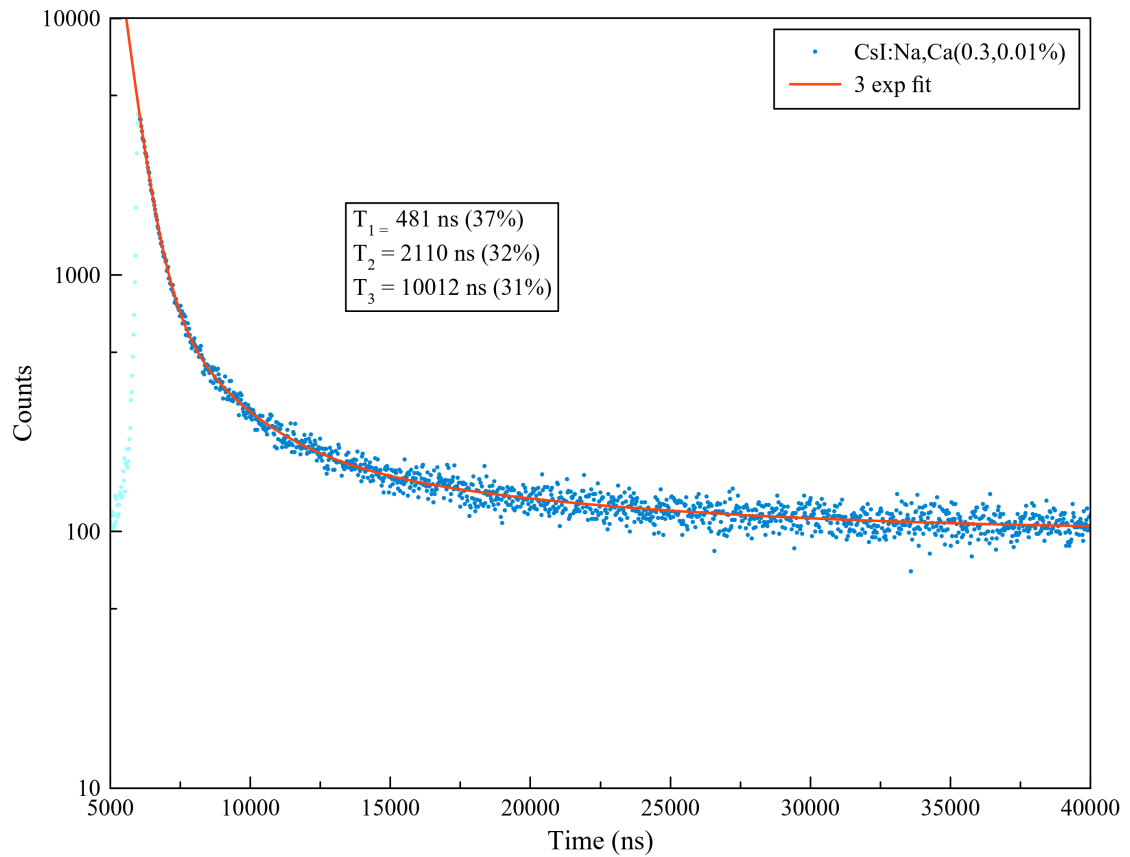


Figure 3.37: CsI:Na,Ca(0.3,0.01)% scintillation decay time

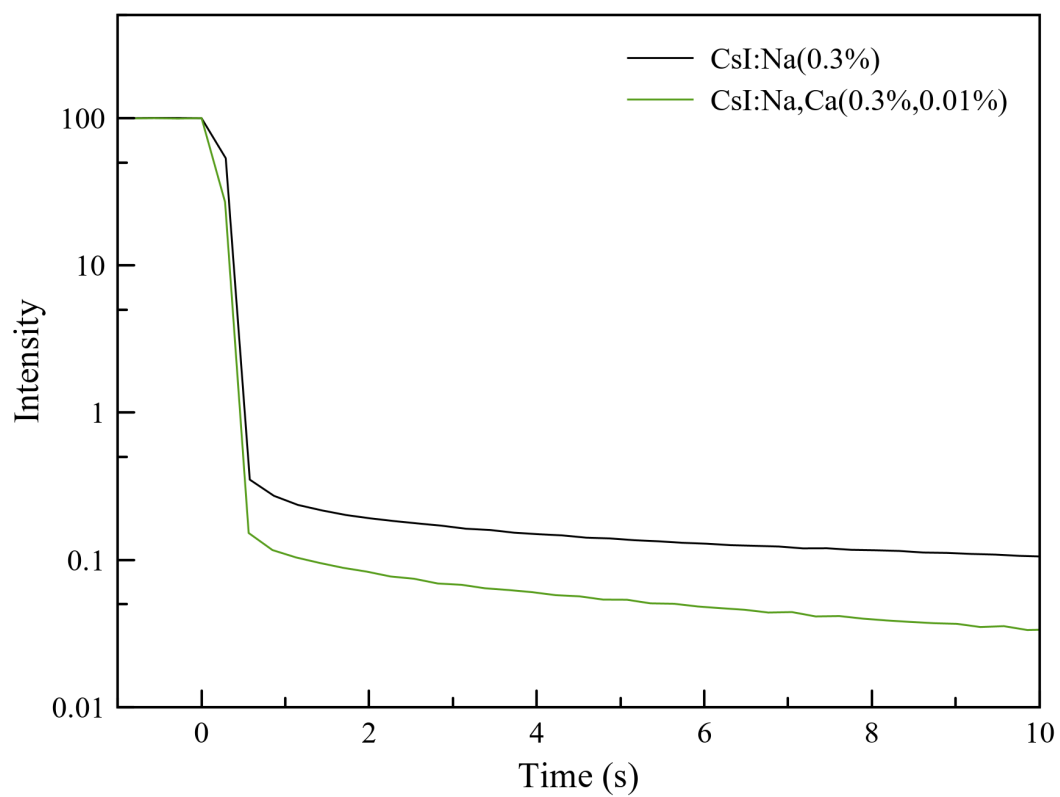


Figure 3.38: CsI:Na,Ca(0.3,0.01)% afterglow compared to afterglow of CsI:Na

3.6 CsI:Na,Sr Crystals

3.6.1 Crystal Growth and Quality

Two crystals were grown for the codoping study, one crystal with a codopant concentration of 0.1% Sr and 0.01% Sr. The codoped crystals were grown via the Bridgman boat growth technique. The crystals were grown at a rate of 2 mm per hour, and cooled over a period of 24 hours. Upon removal from the ampoule, the Sr codoped crystals appeared to be colorless and crack free. It was found upon cutting and polishing that a small pink region appeared on the periphery of each slice.

3.6.2 Scintillation Properties of CsI:Na,Sr

The radioluminescence spectra of CsI:Na,Sr samples were measured and the results are shown in Figure 3.41. According to the data, there is no meaningful change to the radioluminescence spectra.

The light yield of Sr doped CsI:Na was measured and the results are shown in Figure 3.43. The light yield is significantly higher for the lightly Sr doped sample, but the spectroscopic quality suffers. On the contrary, CsI:Na,Sr(0.3,0.1%) did not improve the light yield, but the light yield uniformity of the sample was improved along with the spectroscopic quality with a small second photopeak component within slice 6. The scintillation decay times of CsI:Na,Sr scintillators are shown in Figure 3.44 and 3.45. The timing of the CsI:Na,Sr scintillators does not deviate greatly from the decay components of other codoped CsI:Na samples, but the long component of CsI:Na,Sr(0.3,0.01%) is significantly longer than the other samples. Like the other codoped samples, the afterglow of CsI:Na,Sr crystals is substantially reduced on the timescale of seconds.

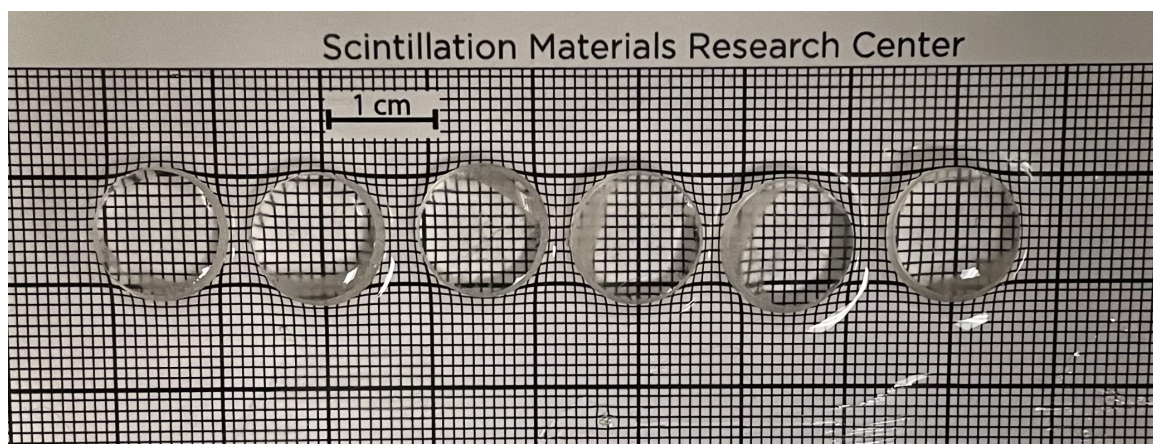


Figure 3.39: CsI:Na,Sr(0.3,0.01)% crystal slabs with slabs ordered left to right in ascending order

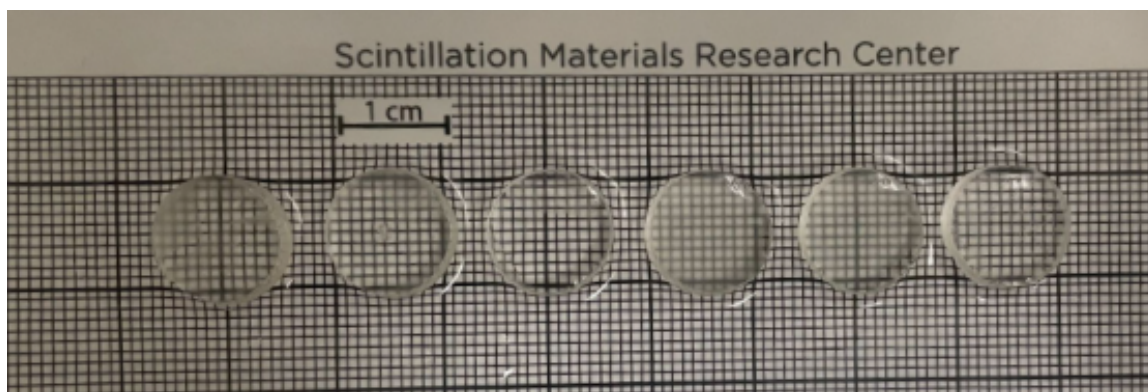


Figure 3.40: CsI:Na,Sr(0.3,0.1)% crystal slabs with slabs ordered left to right in ascending order

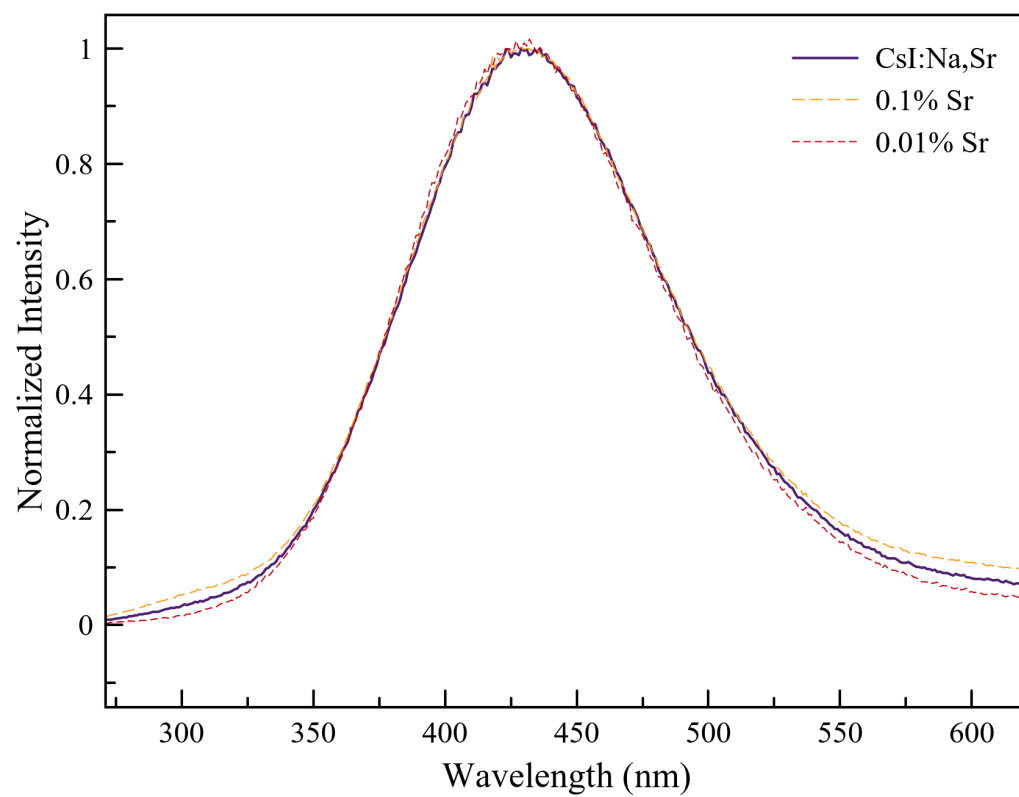


Figure 3.41: CsI:Na,Sr(0.3,0.01)% radioluminescence spectra

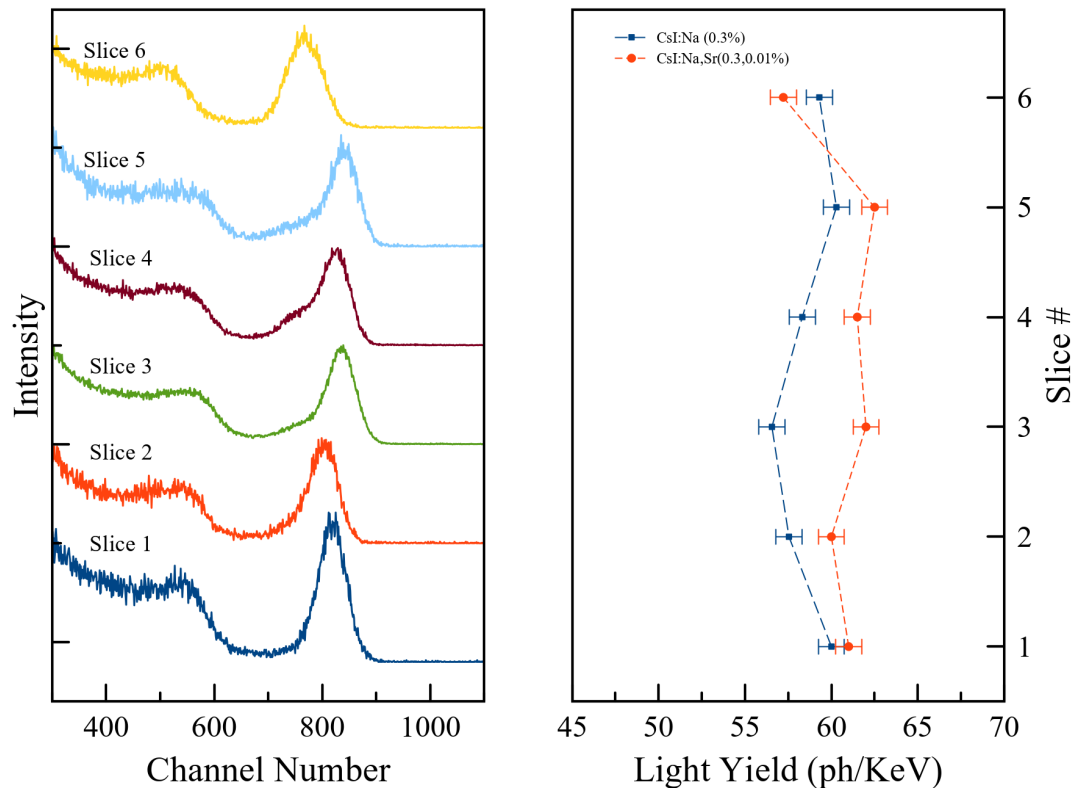


Figure 3.42: Pulse height spectra and light yield for CsI:Na,Sr(0.3,0.01%)

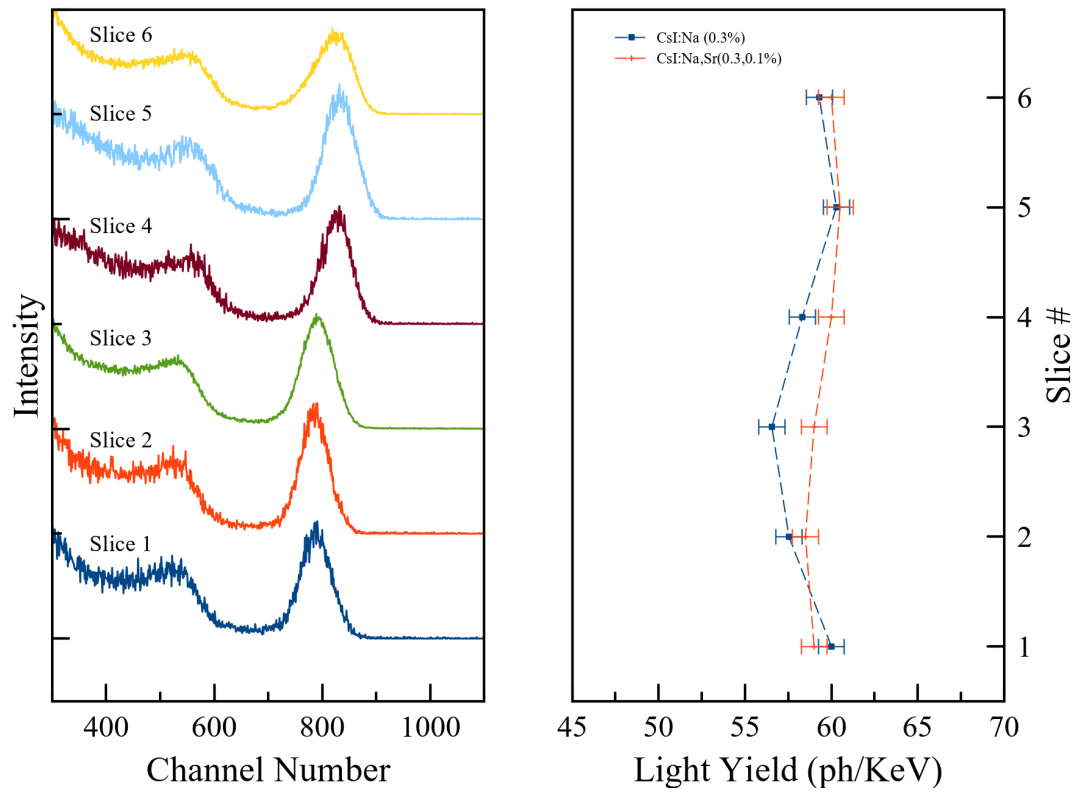


Figure 3.43: Pulse height spectra and light yield for CsI:Na,Sr(0.3, 0.1%)

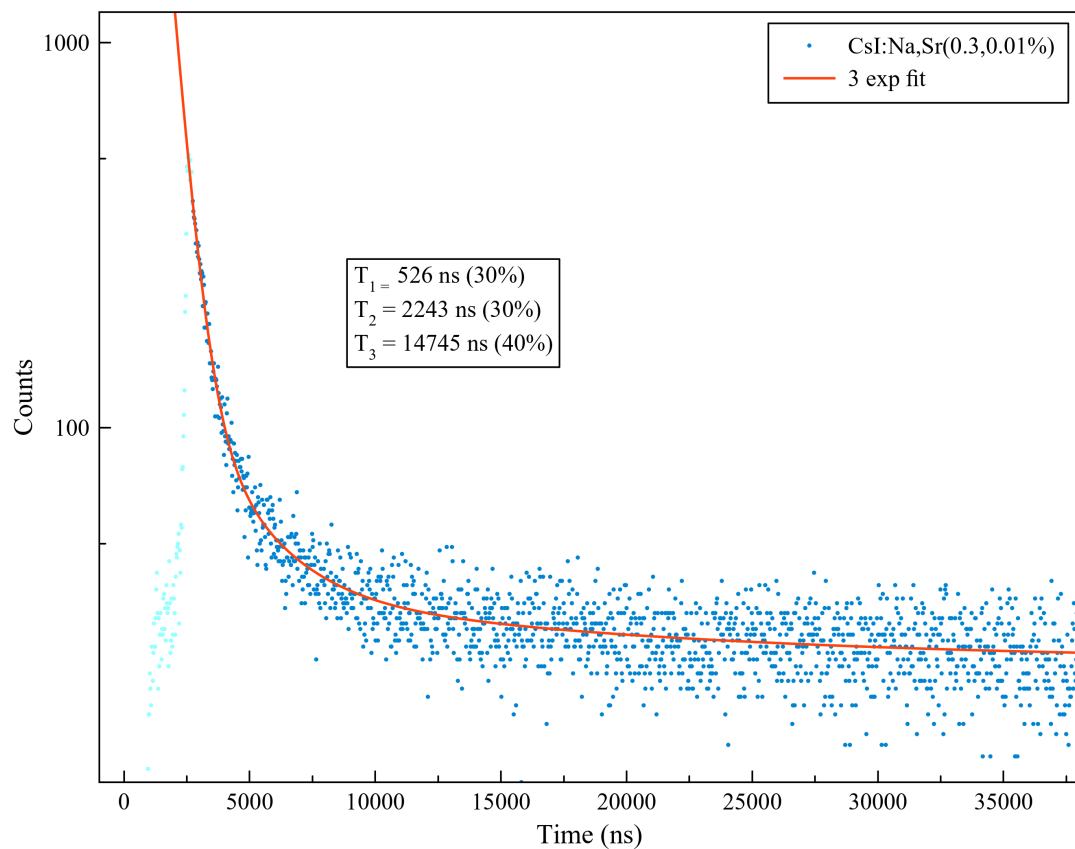


Figure 3.44: CsI:Na,Sr(0.3,0.01%) scintillation decay plot and components

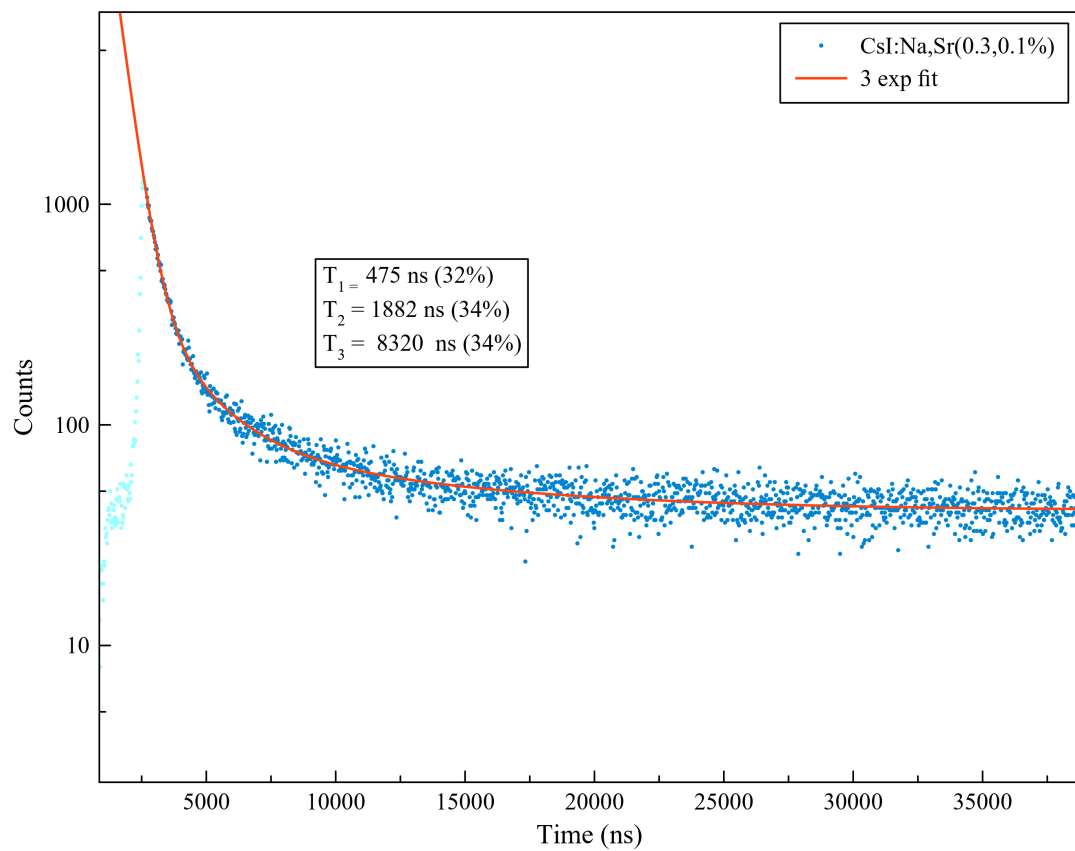


Figure 3.45: CsI:Na,Sr(0.3,0.1%) scintillation decay plot and components

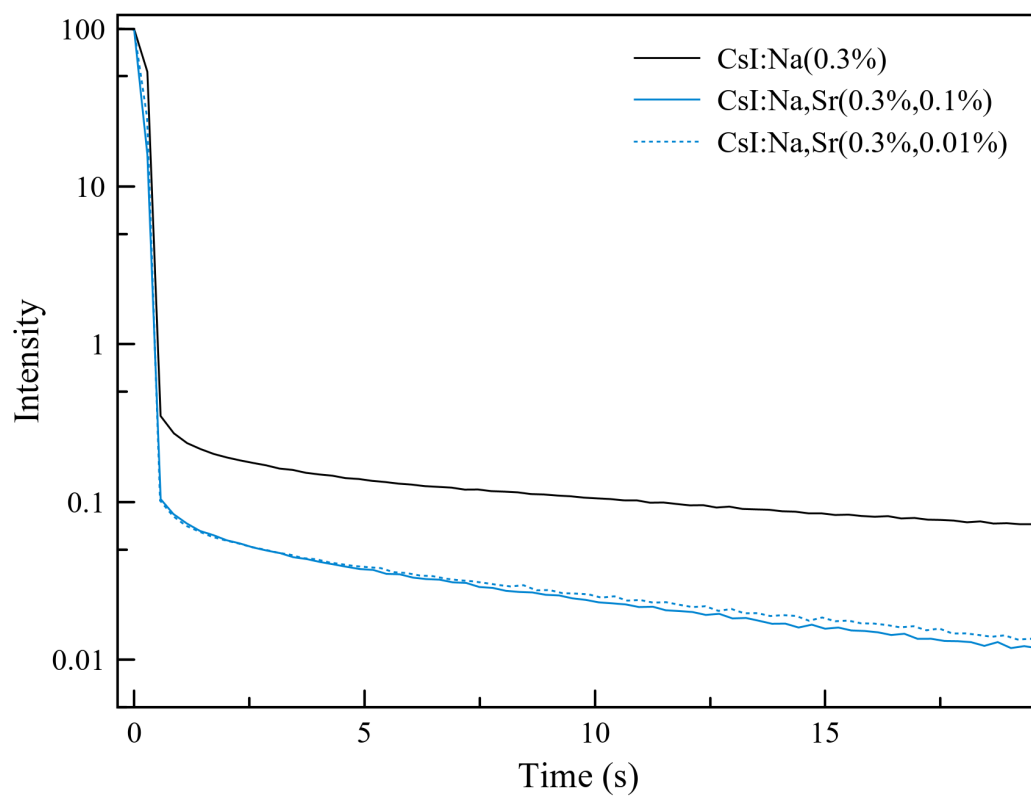


Figure 3.46: CsI:Na,Sr crystal afterglows compared to CsI:Na reference.

3.7 CsI:Na,Rb Crystals

3.7.1 Crystal Growth and Quality

Crystals of Rb codoped CsI:Na are shown in Figure 3.47. The crystals appeared mostly colorless and clear, but had what appeared to be extensive cracking, much like the CsI:Na,Ca(0.3,0.3)% boule. Large sections of the 0.1% Rb crystal sheared off during the cutting and polishing phase which is evident by the semi-circular shapes of slices 3 and 4 in Figure 3.47. The regions that sheared off were heavily cracked and were densely populated by bubble-like defects but was not colored, unlike similar regions seen in the Eu codoped crystals.

3.7.2 Scintillation Properties of CsI:Na,Rb Scintillators

The radioluminescence spectra for CsI:Na,Rb samples are presented in Figure 3.49. There is no observable difference in the radioluminescence spectra.

The light yield and pulse height spectra are shown in figures 3.50 and 3.51. The pulse height spectra indicates inhomogeneity within the crystal by the presence of double peaks. Crystal slabs that had opaque or impurity rich sections have a more prominent double photopeak like those seen on slice 6 of Figure 3.51. The light yield of CsI:Na,Rb(0.3,0.01%) is slightly higher than the reference crystal, but there is a significant difference in light yield from slice to slice.

The scintillation decay of CsI:Na,Rb is presented in Figures 3.52 and 3.53. Both concentrations of Rb in the crystal enhance the longer scintillation decay components.

The afterglow of Rb codoped CsI:Na is shown in Figure 3.54. Both concentrations of Rb codoped CsI:Na reduce the afterglow by about an order of magnitude, and have approximately the same afterglow reduction. The cause of afterglow reduction is unknown, but thermoluminescence studies planned for the future should give more insight on how afterglow is reduced by Rb codoping.

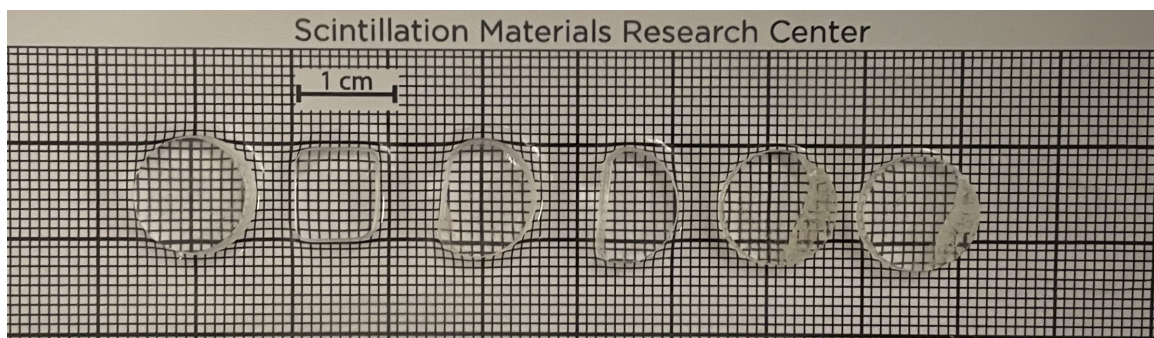


Figure 3.47: CsI:Na,Rb(0.3,0.1)% crystal slabs with slabs ordered left to right in ascending order

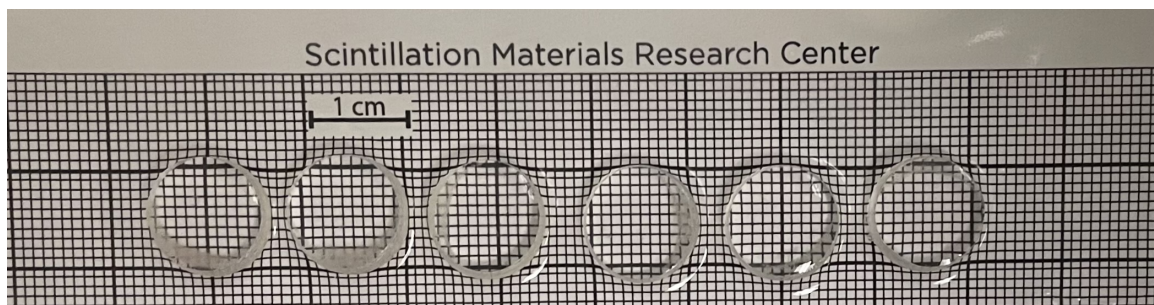


Figure 3.48: CsI:Na,Rb(0.3,0.01)% crystal slabs with slabs ordered left to right in ascending order

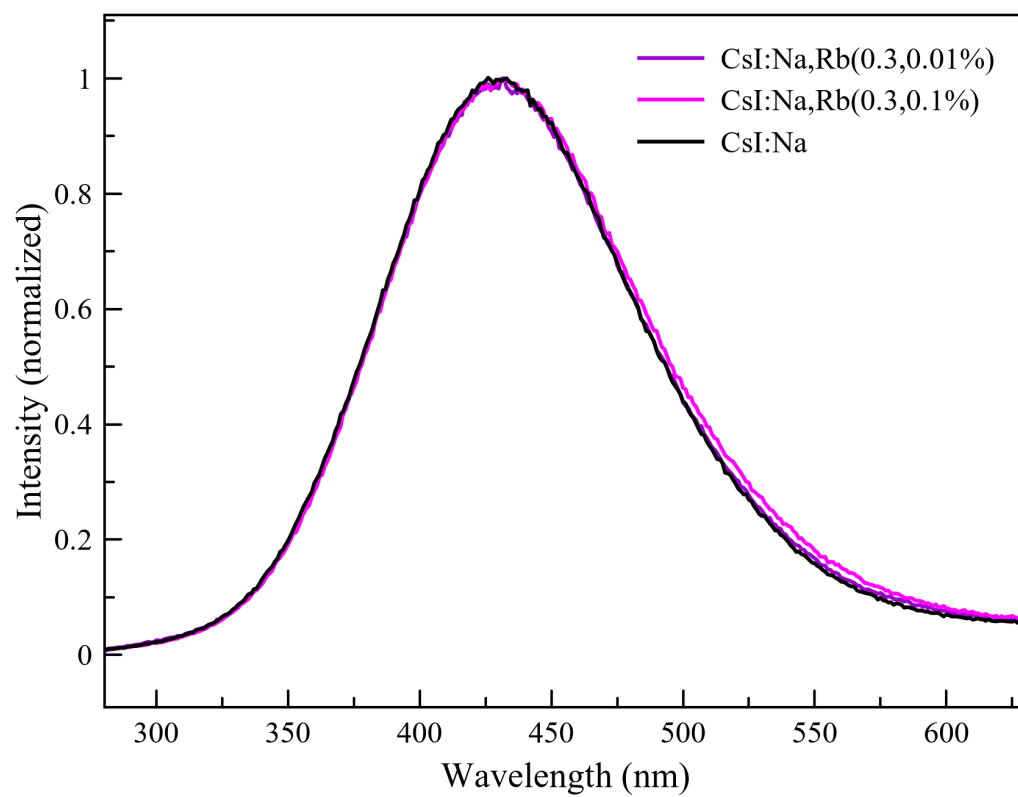


Figure 3.49: CsI:Na,Rb(0.3,0.01)% afterglow compared to CsI:Na reference.

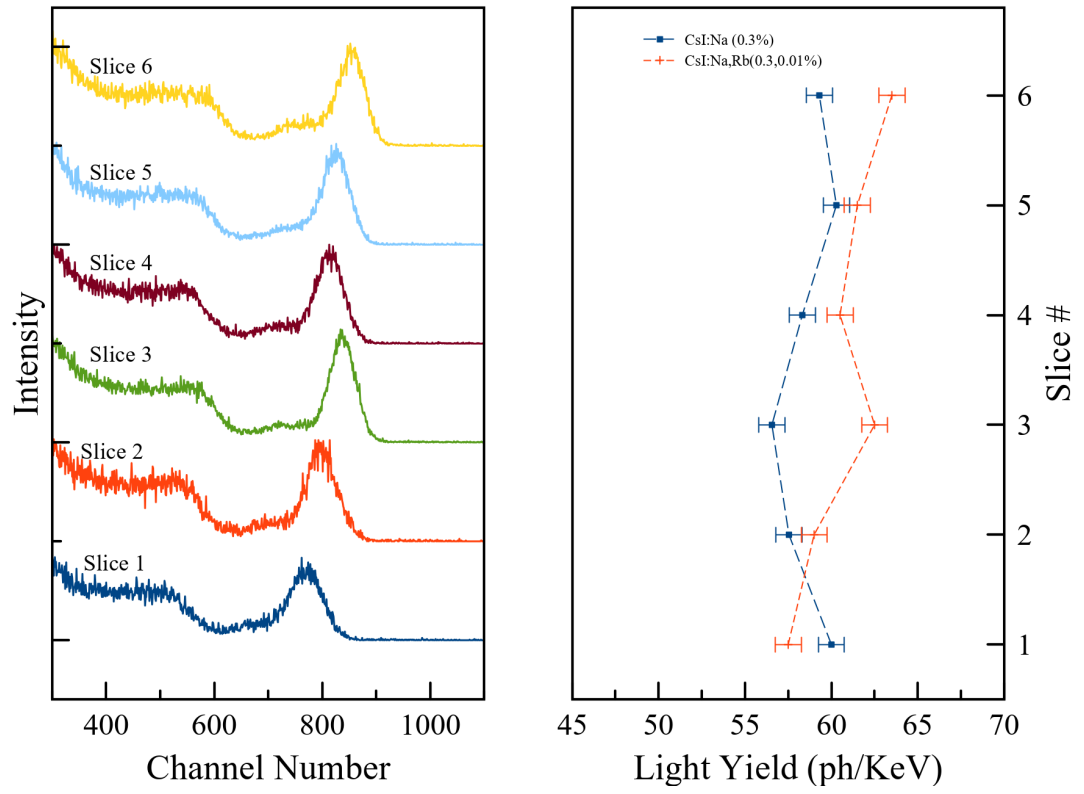


Figure 3.50: CsI:Na,Rb(0.3,0.01)% light yield as a function along crystal boule

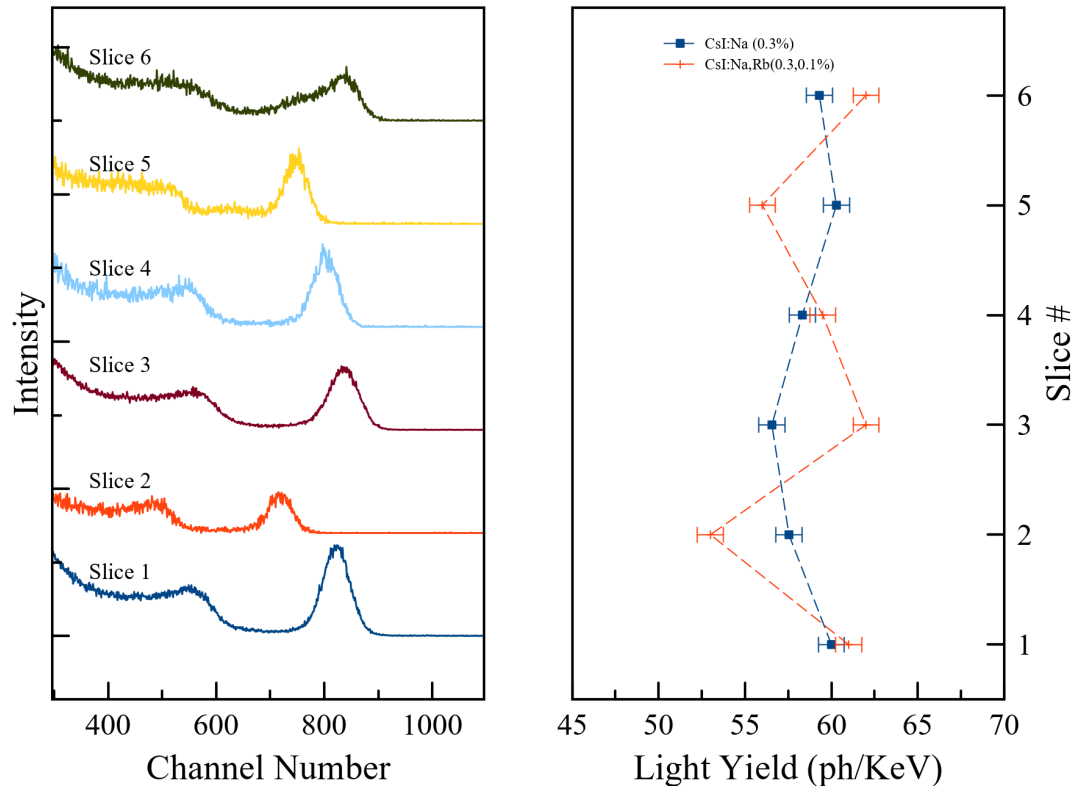


Figure 3.51: CsI:Na,Rb(0.3,0.01)% light yield as a function along crystal boule

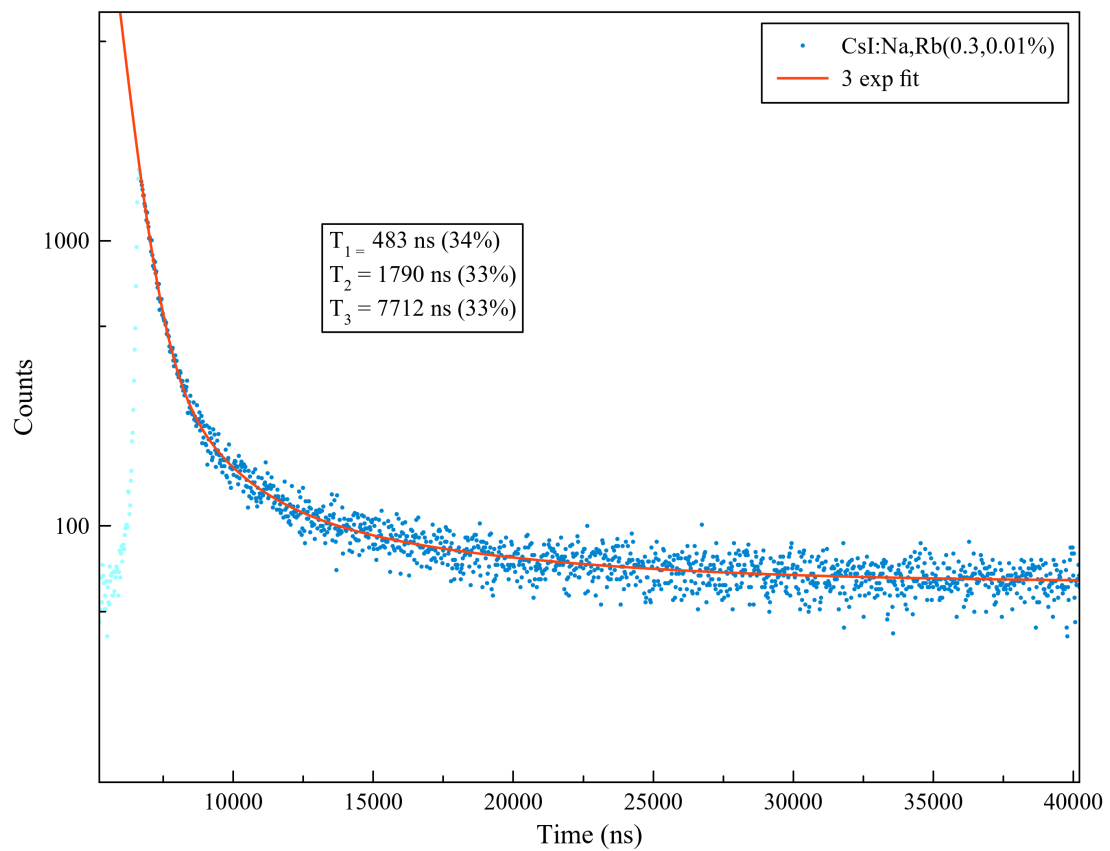


Figure 3.52: CsI:Na,Rb(0.3,0.01)% light yield as a function along crystal boule

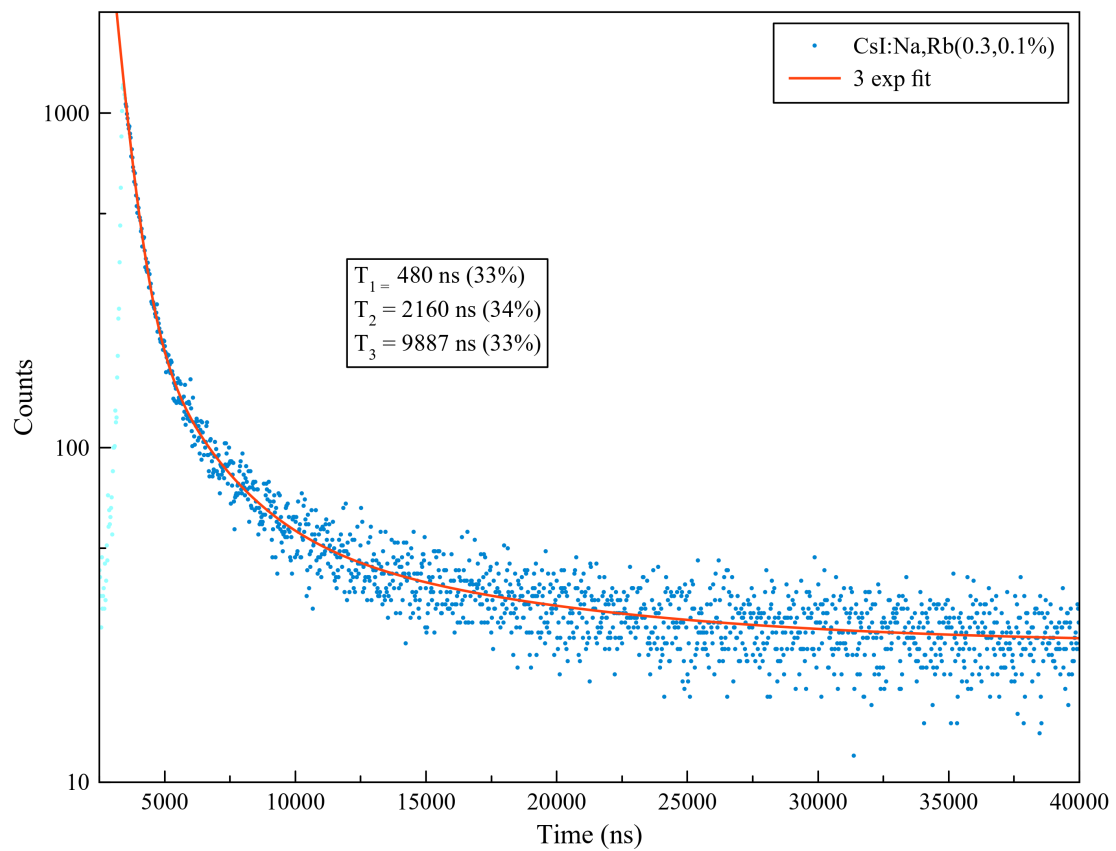


Figure 3.53: CsI:Na,Rb(0.3,0.01)% light yield as a function along crystal boule

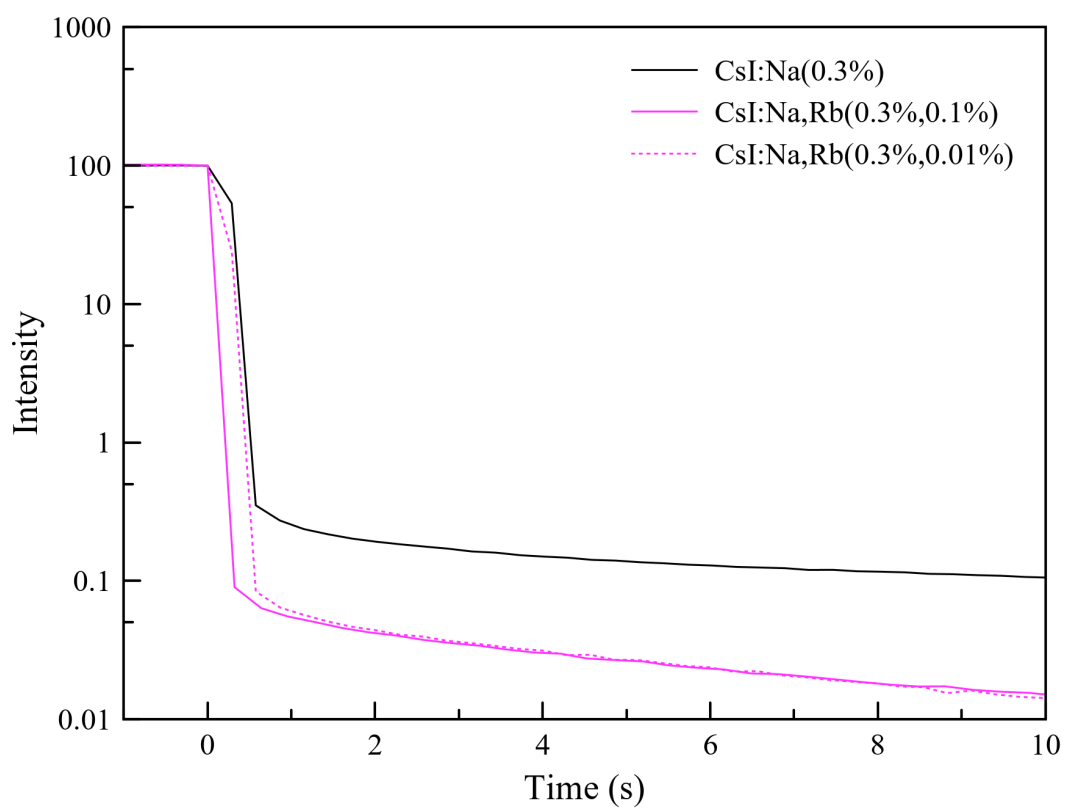


Figure 3.54: CsI:Na,Rb(0.3,0.01)% afterglow compared to CsI:Na reference.

Chapter 4

Conclusions

In this work, the effects of codoping on the scintillation properties of CsI:Na were explored. The resulting crystals proved to be generally of good optical quality, but improvements could be made on the crystal growth procedure. Instead of using the boat growth method, the individual-crystal growth method would be used to ensure a uniform radial thermal gradient which would yield more uniform crystals. Another potential improvement to the crystal growth technique is an active melt mixing procedure using accelerated crucible rotation technique. Ensuring effective mixing of the melt will produce a more uniform crystal, which should improve its optical and spectroscopic qualities.

The scintillation properties are summarized in Table 4. A remarkable trend in this data is the reduction of afterglow with nearly every codoped sample. We believe this is associated with the suppression of hole traps and electron scavenging as described in [35], but more work must be done to determine the exact mechanisms of afterglow reduction. To determine the afterglow reduction mechanism, thermoluminescence studies will be performed so the effects of codoping on the trap structure of CsI:Na can be observed. Another interesting effect on the scintillation properties was an increase in light yield for Yb^{2+} , Sr^{2+} , and Ca^{2+} . Of these codopants, Yb as a codopant shows the most promise as an improvement for the light yield of CsI:Na. In general, the

samples with a smaller concentration of codopant (0.01% codoped samples) performed much better than the more heavily doped samples in light yield. The underperforming light yield of the heavily doped samples could be explained by the poor codopant segregation that causes defects that are detrimental to the transparency / scintillation mechanism like those seen in Figure 3.6. However, more work must be performed to identify the mechanics of scintillation effects caused by codoping. The decay time of CsI:Na scintillators was lengthened significantly for most codoped samples, which is interesting considering the improvements to afterglow.

Table 4.1: Table of scintillation properties of codoped CsI:Na scintillators.

Composition	LY (ph/MeV)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	λ_{em}	Afterglow (% I_0 at s)
CsI:Na(0.3%)	59,000	511 (73%)	2119 (15%)	9713 (12%)	430	0.27
CsI:Na, Eu(0.3%, 0.1%)	59,000	510 (78%)	1912 (13%)	8746 (9%)	450	0.28
CsI:Na, Eu(0.3%, 0.01%)	59,000	442 (28%)	900 (34%)	7910 (38%)	450	0.15
CsI:Na, Yb(0.3%, 0.1%)	63,000	465 (33%)	1987 (34%)	8830 (33%)	450	0.15
CsI:Na, Yb(0.3%, 0.01%)	65,000	364 (15%)	788 (35%)	4878 (50%)	430	0.08
CsI:Na, Ca(0.3%, 0.01%)	63,700	481 (37%)	2110 (32%)	10012 (31%)	430	0.11
CsI:Na, Sr(0.3%, 0.1%)	59,000	540 (4%)	2910 (26%)	38918 (70%)	430	0.08
CsI:Na, Sr(0.3%, 0.01%)	62,500	526 (6%)	2234 (32%)	14512 (62%)	430	0.08
CsI:Na, Sm(0.3%, 0.1%)	37,500	420 (23%)	1355 (32%)	6796 (45%)	430	0.03
CsI:Na, Sm(0.3%, 0.01%)	52,000	475 (32%)	1922 (32%)	9124 (36%)	430	0.04
CsI:Na, Rb(0.3%, 0.1%)	62,000	480 (33%)	2160 (33%)	9887 (33%)	430	0.06
CsI:Na Rb(0.3%, 0.01%)	63,500	483 (34%)	1790 (33%)	7712 (33%)	430	0.06

Bibliography

- [1] Csi(na)- cesium iodide (sodium). URL https://www.advatech-uk.co.uk/csi_na.html. 34
- [2] C. Amsler, D. Grögler, W. Joffrain, D. Lindelöf, M. Marchesotti, P. Niederberger, H. Pruys, C. Regenfus, P. Riedler, and A. Rotondi. Temperature dependence of pure csi: scintillation light yield and decay time. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 480(2):494–500, 2002. ISSN 0168-9002. doi: [https://doi.org/10.1016/S0168-9002\(01\)01239-6](https://doi.org/10.1016/S0168-9002(01)01239-6). URL <https://www.sciencedirect.com/science/article/pii/S0168900201012396>. 5
- [3] G. Angloher, I. Dafinei, A. Gektin, L. Gironi, C. Gotti, A. Gütlein, D. Hauff, M. Maino, S. Nagorny, S. Nisi, L. Pagnanini, L. Pattavina, G. Pessina, F. Petricca, S. Pirro, F. Pröbst, F. Reindl, K. Schäffner, J. Schieck, W. Seidel, and S. Vasyukov. A csi low-temperature detector for dark matter search. *Astroparticle Physics*, 84:70–77, 2016. ISSN 0927-6505. doi: <https://doi.org/10.1016/j.astropartphys.2016.08.005>. URL <https://www.sciencedirect.com/science/article/pii/S0927650516301189>. 5
- [4] M. Berger, J. Hubbell, S. Seltzer, J. Coursey, and D. Zucker. Xcom: Photon cross section database (version 1.2), 1999-01-01 1999. 5
- [5] P. Bhattacharya, S. Miller, M. Wart, C. Brecher, and V. V. Nagarkar. Bridgman-grown CsI:Tl crystals codoped to suppress afterglow for high-throughput cargo

- p inspection. 10763:70 – 77, 2018. doi: 10.1117/12.2326552. URL
- <https://doi.org/10.1117/12.2326552>
- . 8, 9
- [6] L. M. Bollinger and G. E. Thomas. Measurement of the time dependence of scintillation intensity by a delayed-coincidence method. *Review of Scientific Instruments*, 32(9):1044–1050, 1961. doi: 10.1063/1.1717610. URL <https://doi.org/10.1063/1.1717610>. 27, 28
- [7] C. Brecher, V. Nagarkar, V. Gaysinskiy, S. Miller, and A. Lempicki. Time-resolved studies of the nonexponential decay of csi(tl) after short-pulse x-ray excitation. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 537(1):117–124, 2005. ISSN 0168-9002. doi: <https://doi.org/10.1016/j.nima.2004.07.247>. URL <https://www.sciencedirect.com/science/article/pii/S0168900204017954>. Proceedings of the 7th International Conference on Inorganic Scintillators and their Use in Scientific and Industrial Applications. 8
- [8] C. Brecher, A. Lempicki, S. Miller, J. Glodo, E. Ovechkina, V. Gaysinskiy, V. Nagarkar, and R. Bartram. Suppression of afterglow in csi:tl by codoping with eu2+—i: Experimental. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 558(2):450–457, 2006. ISSN 0168-9002. doi: <https://doi.org/10.1016/j.nima.2005.11.119>. URL <https://www.sciencedirect.com/science/article/pii/S016890020502156X>. 8, 10
- [9] W. Chewpraditkul, L. Swiderski, and M. Moszynski. Light yield non-proportionality and intrinsic energy resolution of doped csi scintillators. *Nukleonika*, 53:51, 01 2008. 11
- [10] W. Chewpraditkul, L. Swiderski, M. Moszynski, T. Szczesniak, A. Syntfeld-Kazuch, C. Wanarak, and P. Limsuwan. Scintillation properties of luag:ce, yag:ce

- and lyso:ce crystals for gamma-ray detection. *IEEE Transactions on Nuclear Science*, 56(6):3800–3805, 2009. doi: 10.1109/TNS.2009.2033994. 4
- [11] C. J. Crannell, R. J. Kurz, and W. Viehmann. Characteristics of cesium iodide for use as a particle discriminator for high-energy cosmic rays. *Nucl. Instrum. Methods, v. 115, no. 1, pp. 253-261*. doi: 10.1016/0029-554X(74)90454-6. URL <https://www.osti.gov/biblio/4323840>. 5
- [12] J. de Haas, P. Dorenbos, and C. van Eijk. Measuring the absolute light yield of scintillators. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 537(1):97–100, 2005. ISSN 0168-9002. doi: <https://doi.org/10.1016/j.nima.2004.07.243>. URL <https://www.sciencedirect.com/science/article/pii/S0168900204017917>. Proceedings of the 7th International Conference on Inorganic Scintillators and their Use in Scientific and Industrial Applications. 25
- [13] H. Dietrich and R. Murray. Kinetics of the diffusion of self-trapped holes in alkali halide scintillators. *Journal of Luminescence*, 5(3):155–170, 1972. ISSN 0022-2313. doi: [https://doi.org/10.1016/0022-2313\(72\)90039-7](https://doi.org/10.1016/0022-2313(72)90039-7). URL <https://www.sciencedirect.com/science/article/pii/0022231372900397>. 5
- [14] W. C. Kaiser. Scintillation spectrometry the state of the art. *Analytical Chemistry*, 38(11):27A–39A, 1966. 6
- [15] E. Khodadoost and M. A. Araghi. Scintillation response of europium and indium-co-doped csi(na) single crystal under the exposure of gamma-ray. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 942:162351, 2019. ISSN 0168-9002. doi: <https://doi.org/10.1016/j.nima.2019.162351>. URL <https://www.sciencedirect.com/science/article/pii/S0168900219309313>. 11

- [16] M. J. Kim, H. J. Kim, H. Park, K. Tanida, S. Kim, J. K. Cheon, and K. B. Lee. Scintillation properties of csi:na , ^{133}i crystal. *IEEE Transactions on Nuclear Science*, 60(2):1049–1052, 2013. doi: 10.1109/TNS.2013.2251898. 11
- [17] W. J. C. Koppert, M. M. A. Dietze, S. van der Velden, J. H. L. Steenbergen, and H. W. A. M. de Jong. A comparative study of NaI(tl), CeBr₃, and CZT for use in a real-time simultaneous nuclear and fluoroscopic dual-layer detector. *Physics in Medicine & Biology*, 64(13):135012, jul 2019. doi: 10.1088/1361-6560/ab267c. URL <https://doi.org/10.1088/1361-6560/ab267c>. 4
- [18] P. Lecoq. Development of new scintillators for medical applications. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 809:130–139, 2016. ISSN 0168-9002. doi: <https://doi.org/10.1016/j.nima.2015.08.041>. URL <https://www.sciencedirect.com/science/article/pii/S0168900215009754>. Advances in detectors and applications for medicine. 3, 4, 5
- [19] V. B. Mikhailik, V. Kapustyanyk, V. Tsybulskyi, V. Rudyk, and H. Kraus. Luminescence and scintillation properties of csi : A potential cryogenic scintillator. *physica status solidi (b)*, 252(4):804–810, 2015. doi: <https://doi.org/10.1002/pssb.201451464>. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/pssb.201451464>. 5
- [20] S. L. Molodtsov, A. Puschmann, C. Laubschat, G. Kaendl, and V. K. Adamchuk. Comparative study of unoccupied electronic states in insulators: Csi . *Phys. Rev. B*, 44:1333–1336, Jul 1991. doi: 10.1103/PhysRevB.44.1333. URL <https://link.aps.org/doi/10.1103/PhysRevB.44.1333>. 5
- [21] R. Monnier. Electron trapping by substitutional alkali ion impurities in csi . *Solid State Communications*, 19(7):681–683, 1976. ISSN 0038-1098. doi: [https://doi.org/10.1016/0038-1098\(76\)90038-1](https://doi.org/10.1016/0038-1098(76)90038-1).

- //doi.org/10.1016/0038-1098(76)91104-2. URL <https://www.sciencedirect.com/science/article/pii/0038109876911042>. 6
- [22] M. Moszyński, C. Gresset, J. Vacher, and R. Odru. Timing properties of bgo scintillator. *Nuclear Instruments and Methods in Physics Research*, 188(2): 403–409, 1981. ISSN 0167-5087. doi: [https://doi.org/10.1016/0029-554X\(81\)90521-8](https://doi.org/10.1016/0029-554X(81)90521-8). URL <https://www.sciencedirect.com/science/article/pii/0029554X81905218>. 4
- [23] C. K. Ong, K. S. Song, R. Monnier, and A. M. Stoneham. Electronic structure and luminescence of CsI:na. *Journal of Physics C: Solid State Physics*, 12(21): 4641–4646, nov 1979. doi: 10.1088/0022-3719/12/21/028. URL <https://doi.org/10.1088/0022-3719/12/21/028>. 6
- [24] X. Ouyang, B. Liu, X. Xiang, L. Chen, M. Xu, X. Song, J. Ruan, J. Liu, C. Chen, Z. Zhu, and Y. Li. Enhanced light output of csi(na) scintillators by photonic crystals. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 969:164007, 2020. ISSN 0168-9002. doi: <https://doi.org/10.1016/j.nima.2020.164007>. URL <https://www.sciencedirect.com/science/article/pii/S0168900220304599>. 6
- [25] E. Ovechkina, V. Gaysinskiy, S. Miller, C. Brecher, A. Lempicki, and V. Nagarkar. Multiple doping of csi:tl crystals and its effect on afterglow. *Radiation Measurements*, 42(4):541–544, 2007. ISSN 1350-4487. doi: <https://doi.org/10.1016/j.radmeas.2007.01.086>. URL <https://www.sciencedirect.com/science/article/pii/S1350448707000571>. Proceedings of the 6th European Conference on Luminescent Detectors and Transformers of Ionizing Radiation (LUMDETR 2006). 6
- [26] E. Ovechkina, V. Gaysinskiy, S. Miller, C. Brecher, A. Lempicki, and V. Nagarkar. Multiple doping of csi:tl crystals and its effect on afterglow.

- Radiation Measurements*, 42(4):541–544, 2007. ISSN 1350-4487. doi: <https://doi.org/10.1016/j.radmeas.2007.01.086>. URL <https://www.sciencedirect.com/science/article/pii/S1350448707000571>. Proceedings of the 6th European Conference on Luminescent Detectors and Transformers of Ionizing Radiation (LUMDETR 2006). 4, 8
- [27] P. A. Rodnyj. *Physical Processes in inorganic scintillators*. CRC Press, 1997. 4
- [28] P. Sibczynski, A. Broslawski, A. Gojska, V. Kiptily, S. Korolczuk, R. Kwiatkowski, S. Mianowski, M. Moszyński, J. Rządkiwicz, L. Swiderski, A. Szydlowski, and I. Zychor. Characterization of some modern scintillators recommended for use on large fusion facilities in γ -ray spectroscopy and tomographic measurements of γ -emission profiles. *Nukleonika*, 62(3):223–228, 2017. doi: [doi:10.1515/nuka-2017-0032](https://doi.org/10.1515/nuka-2017-0032). URL <https://doi.org/10.1515/nuka-2017-0032>. 5
- [29] K. Sonnenberg and E. Küssel. Developments in vertical bridgman growth of large diameter gaas. *III-Vs Review*, 10(5):30–34, 1997. ISSN 0961-1290. doi: [https://doi.org/10.1016/S0961-1290\(97\)81284-7](https://doi.org/10.1016/S0961-1290(97)81284-7). URL <https://www.sciencedirect.com/science/article/pii/S0961129097812847>. 12
- [30] Suerfu. *Developing Ultra Low-Background Sodium-Iodide Crystal Detector for Dark Matter Searches*. PhD thesis, 2018. 14
- [31] D. Totsuka, T. Yanagida, Y. Fujimoto, Y. Yokota, F. Moretti, A. Vedda, and A. Yoshikawa. Afterglow suppression by codoping with bi in CsI:tl crystal scintillator. *Applied Physics Express*, 5(5):052601, apr 2012. doi: [10.1143/apex.5.052601](https://doi.org/10.1143/apex.5.052601). URL <https://doi.org/10.1143/apex.5.052601>. 8
- [32] C. E. Tyner and H. G. Drickamer. Studies of the luminescence efficiency of tungstate and molybdate phosphors as a function of temperature and high

- pressure. *The Journal of Chemical Physics*, 67(9):4103–4115, 1977. doi: 10.1063/1.435387. URL <https://aip.scitation.org/doi/abs/10.1063/1.435387>. 4
- [33] W. Van Sciver and R. Hofstadter. Scintillations in thallium-activated CaI_2 and CsI . *Phys. Rev.*, 84:1062–1063, Dec 1951. doi: 10.1103/PhysRev.84.1062.2. URL <https://link.aps.org/doi/10.1103/PhysRev.84.1062.2>. 6
- [34] I. Wadeng, P. Saengkaew, V. Yordsri, C. Thanachayanont, and N. Nuntawong. Growth and characterization of calcium-doped cesium iodide (CsI:Ca) optical crystals for radiation detection. In F. Baldini, J. Homola, and R. A. Lieberman, editors, *Optical Sensors 2019*, volume 11028, pages 550 – 560. International Society for Optics and Photonics, SPIE, 2019. doi: 10.1117/12.2523311. URL <https://doi.org/10.1117/12.2523311>. 5
- [35] Y. Wu, G. Ren, M. Nikl, X. Chen, D. Ding, H. Li, S. Pan, and F. Yang. $\text{CsI:tl+},\text{yb}^{2+}$: ultra-high light yield scintillator with reduced afterglow. *CrystEngComm*, 16:3312–3317, 2014. doi: 10.1039/C3CE42645A. URL <http://dx.doi.org/10.1039/C3CE42645A>. 5, 6, 8, 97
- [36] P. Yang, C. D. Harmon, F. P. Doty, and J. A. Ohlhausen. Effect of humidity on scintillation performance in Na and Tl activated CsI crystals. *IEEE Transactions on Nuclear Science*, 61:1024–1031, 2014. 34

Appendix

Appendix A

A.1 Development of an Accelerated Crucible Rotation Technique Mechanism for Vertical Bridgman Growth

Accelerated Crucible Rotation Technique (ACRT) is a method by which the crystal charge is continually mixed throughout the crystal growth by repeatedly accelerating the charge through rotation. This method was originally designed to address challenges with the crystal growth of CdHgTe, and there has been extensive experimental and computational work on the effects of ACRT on crystal growth ?? ?? The results of Capper and Coates's experiments and simulations showed that crystal quality could be improved, and dopant segregation could be mitigated.

The SMRC became interested in the use of ACRT for its scintillator crystal growth projects. One of the key elements of research at the SMRC is the scale up growth of novel scintillator materials, which often proves to be very difficult due to non-uniformity and defects. Therefore, an ACRT system was designed for vertical Bridgman growth of scintillating materials.

The design of an ACRT system is shown in Figure [A.1](#). In this design, the ampoule is attached to a long quartz stir shaft that is coupled to a NEMA-17 stepper motor by a custom made shaft coupler. The shaft coupler has two bore holes: one 5 mm

bore for the shaft and one 8 mm bore for quartz stir rod. The quartz stir rod has dimples pressed into the sides that allow the weight of the ampoule to be loaded onto a group of soft-tipped set screws that firmly hold the shaft in place. Once the stir shaft is secured to the motor shaft, another set of alignment adjustment screws are used to straighten the quartz rod. The alignment of the quartz rod to the motor shaft takes several tries, but can be aligned with great accuracy. Proper alignment is required such that the ampoule does not precess within the furnace. An ampoule that precesses within the furnace is at risk of coliding with the interior of the furnace, which could cause damage to the furnace or damage to the ampoule. The stepper motor is an Adafruit stepper motor that is connected to a Adafruit Motor Shield V2 Stepper driver, and an open source control package AccelStep is used as the control code.

The ACRT system was manufactured and tested on a vertical Bridgman furnace at the SMRC. The prototype system is shown in figure [A.2](#). The numbering on the side of the coupler aids the user in the alignment of the quartz stir shaft.

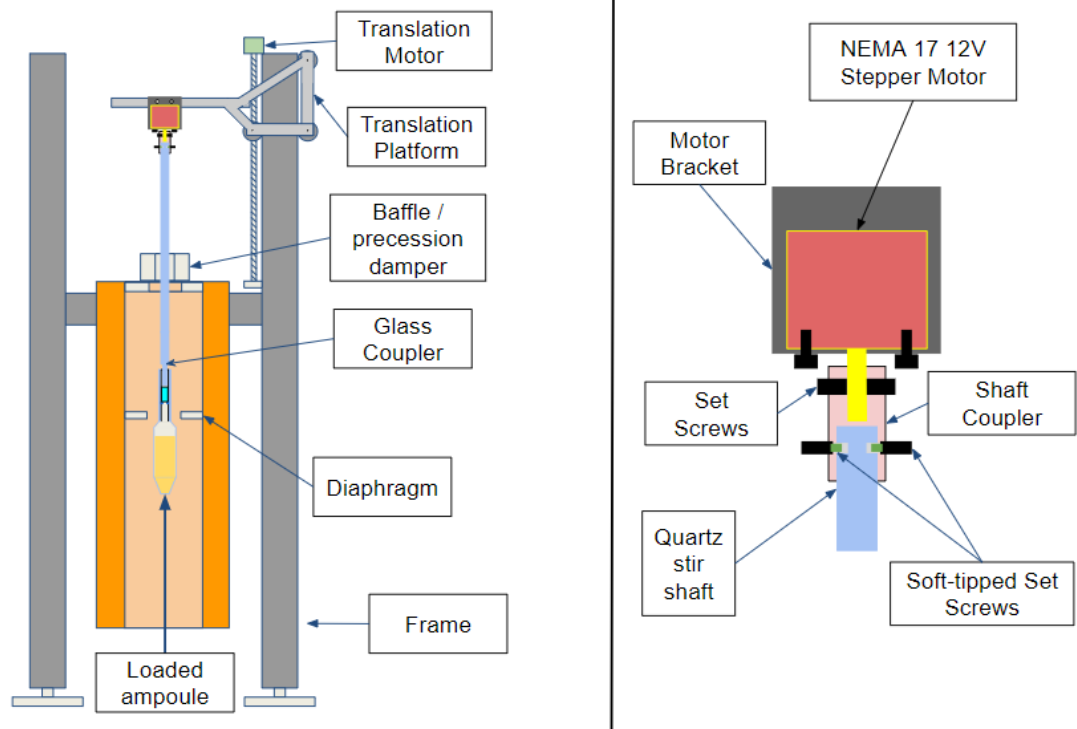


Figure A.1: Diagram of ACRT System implemented at SMRC



Figure A.2: Diagram of pulse height spectra setup.

A.2 Measurement of Vibrations on a Bridgman Furnace

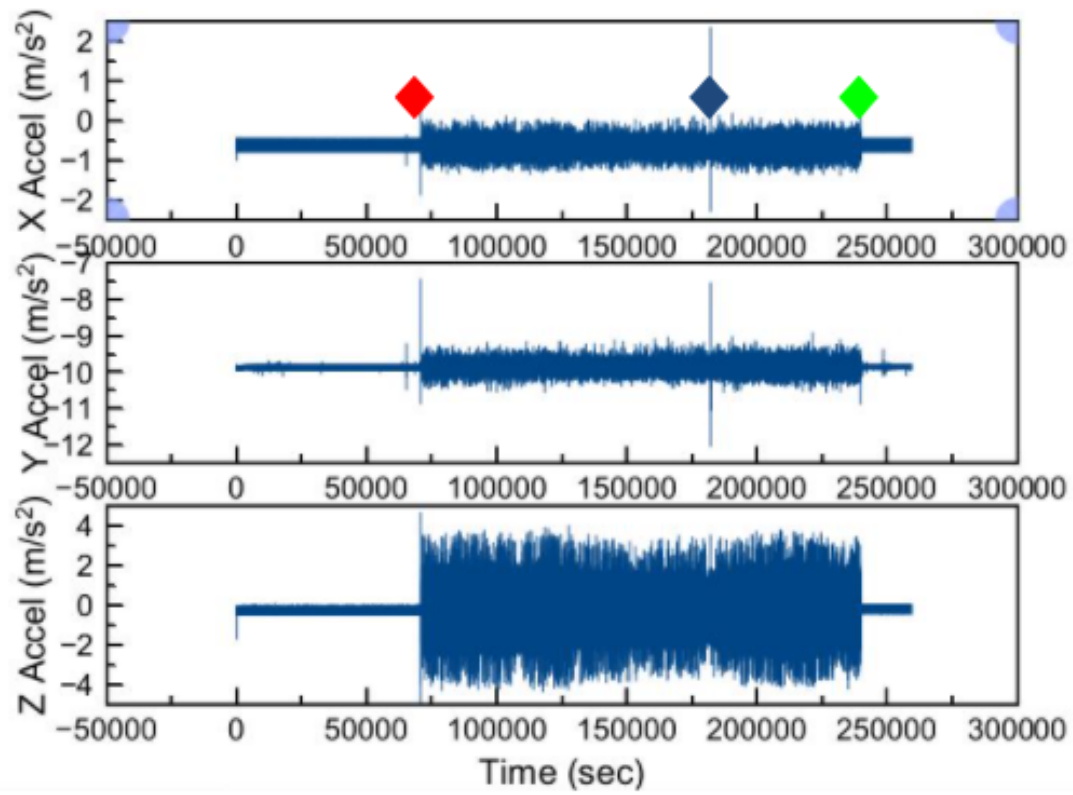
Crystal growth is often referred to as an art form, and for good reason. There are dozens of crystal growth parameters that can be tweaked and modified to produce high quality crystals. However, the effect of environmental vibrations on crystal growth have not been explored.

To collect data on the vibrations experienced by a charge during crystal growth, an arduino-driven LSM9DS1 inertial measurement unit (IMU) was used. A 3D printed plate was created to mechanically couple the IMU to furnace frames. The plate and sensor can be seen in Figure [A.3](#).

The plate and sensor were then attached to a furnace frame and a crystal growth was monitored. The results of this experiment are shown in Figure [A.4](#). In this figure, the data presented before the red mark was around a baseline measurement, and represents noise. However, data presented after the red mark corresponds exactly to the time at which furnace translation was started. The increase in vibration signal seen after the red tick mark was caused by the stepper motor of the translation mechanism. The stepper motor operates in discrete steps at a rate determined by the desired translation speed. These discrete steps cause a short burst of vibration that travels along the entire furnace. These discrete steps can be observed in Figure [A.5](#). The measured vibrations indicate that vibrations within the furnace are underdamped. The data from this device can be used to monitor furnaces for large vibration spikes that may correspond to accidental furnace bumping, door slams, and possibly ampoule explosions. If used on enough crystals, conclusions may be made using an algorithm to determine the overall importance of the vibrational environment around vertical Bridgman growth. The data produced may also be used to simulate fluid flows for melt mixing by ACRT or by



Figure A.3: Picture of the IMU fixed onto its mounting plate



- ◆ Translation started
- ◆ Translation was paused and restarted
- ◆ Translation ended

Figure A.4: Picture of the IMU fixed onto its mounting plate

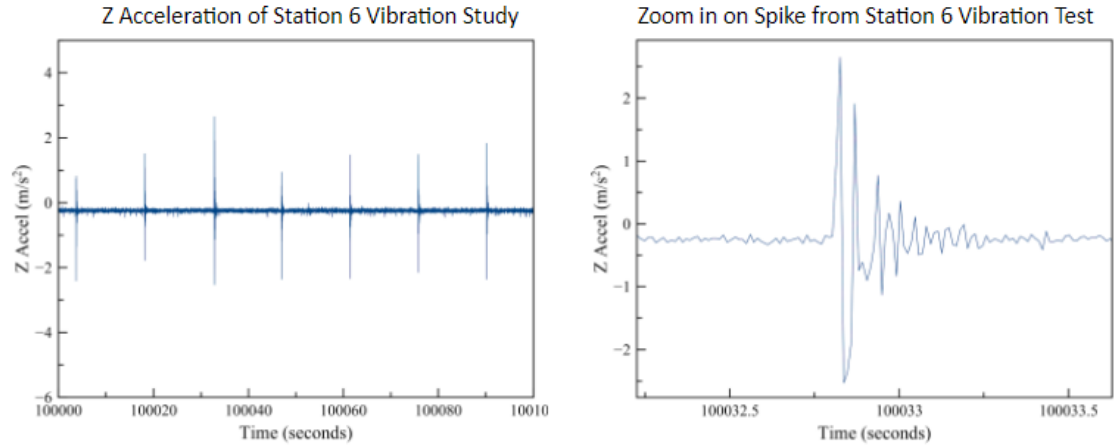


Figure A.5: Vibrations on the furnace on a zoomed in timescales. On the left, vibration spikes can be seen at a regular interval that matches the stepper motor stepping speed. On the right is a zoomed-in plot of a vibration spike, revealing underdamping of vibrations on the furnace.

Vita

Everett Cavanaugh was born on January 31st, 1998 and grew up in Jacksonville, Florida. His mother told him he needed to go to college, or else. He later received his Bachelor of Science in Physics at the University of Alabama in Huntsville after working for four years developing radiation detectors for the detection of Terrestrial Gamma-ray Flashes. Shortly after receiving his degree in physics, he joined the Scintillation Materials Research Center while pursuing a Master of Science degree in medical physics.