Crystal growth of organic compound from the melt

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2014

Hong, I. H. (2014). Crystal growth of organic compound from the melt. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/61851>

<https://doi.org/10.32657/10356/61851>

NANYANG TECHNOLOGICAL UNIVERSITY

**CRYSTAL GROWTH OF ORGANIC
COMPOUND FROM THE MELT**

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2014

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A thesis submitted to the Nanyang Technological
University in partial fulfillment of the requirement for the
degree of Doctor of Philosophy

2014

I. ABSTRACT

Demands on organic scintillator devices for fast neutron detection have been rising in the field of nuclear energy development for industrial usage, biology, chemistry, geology, medicine, and atmospheric science as well as security checks. Organic semiconductors are in principle cheaper, light weight, portable and highly sensitive to large fast neutron fluxes, offering attractive potential as effective radiation detectors. Features present in organic semiconductors which enable fast neutrons detections include the existence of aromatic rings for efficient scintillation; large amount of hydrogen presence for interaction with neutrons; low atomic number constituents, such as carbon or hydrogen, to avoid unnecessary interaction with gamma radiation; a delayed emission to better exhibit energy resolution. Relentless efforts been dedicated to uncover the potential of these scintillation devices (light yield) based on organic single crystals as well as to study their intrinsic charge transport properties so as to harness their application in organic electronics.

Crystal defects and foreign materials do affect the optical as well as electronic properties of organic crystals. Regardless of a high volume of investigations, detailed comprehension of the crystal optical and charge transport behavior and performance remain an unresolved issue for organic based gadgets such as transistors as well as scintillation detectors due to the influence of defects/impurities present in the host. Findings have shown that small concentration of impurities and defects can substantially alter (trapping mechanism) optical/transport characteristics of organic semiconductors. The defects can be caused by the presence of chemical contaminants during the crystal

development process and after the synthesis owing to the thermal deformation and photo chemical reactions.

Since vital to the determination of optical/charge transport mechanism in organic semiconductors is the capability to develop pure, orderly structured molecular crystals for evaluation of photo-luminescence/intrinsic carrier mobility; ultra purification of solid organic crystals consisting of benzene aromatic rings has been a topic of considerable discussion among researchers. Pure organic crystallized materials are therefore the best option to provide efficient scintillation with high light yield and desired carrier mobility in the field of organic transistors (OFETs). Organic single crystals have been commonly attained from the solution, the vapor and the melt phase. Melt growth is more promising than solution growth in that the process takes up less time and free from the issues involving solvent inclusions. Meanwhile, growth of organic crystals from the vapor phase usually results in slow growth of very thin crystals because of the multi-nucleation involved. Therefore, when large single crystals of increased perfection for commercial application are required, these must be grown from the melt.

In this study, single crystals of selenium (proof of concept), anthracene and trans-stilbene up to few centimeters were developed from the melt based on a self established, inexpensive and versatile zone refining apparatus. Platelets cut from these crystals by applying disc cutter (selenium ingot) and thread saw (anthracene together with stilbene ingot) were evaluated for purity and perfection by Powder X-ray Diffraction (XRD), Energy Dispersive X-Ray analysis (EDX), Laser Desorption Ionization-Time of Flight Mass Spectrometry (LDI-ToF MS), Fourier-Transform Infrared Spectroscopy (FT-IR),

Atomic Force Microscopy (AFM) and fluorescence study. Based on the purity analysis, impurity such as carbon within selenium has been effectively segregated. Meanwhile, the outcomes of characterization studies support the purity of organic crystals grown from melt in comparison with solution technique and Bridgman method. In addition, chemical defects (impurities) within commercial anthracene powder such as carbazole and 9,9'Bianthryl have been removed significantly as indicated by LDI-ToF MS analysis. As for trans-stilbene, contaminants such as 1-methylphenanthrene & 2-Phenylindene had been identified. Upon the refinement, both the impurities been minimized within the mid zone of the ingot. The light yield generated within these VZM organic crystals (anthracene and trans-stilbene) upon reduction of the impurities have been greatly improved.

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ACKNOWLEDGEMENT

This thesis final report could not have been possible without the guidance and help given by my supervisor, Professor Christian Kloc. I really appreciate the encouragement and comments given to me in order to make this project a success. I would like to express my gratitude towards my peers, Dr Stevin Pramana, Dr Tan Ke Jie, Dr Toh Minglin, Dr Zhang Keke, Mr Arjun Krishna Kumar and Dr Jiang Hui from School of Materials Science and Engineering for spending their time in assisting the project.

In addition, I would also like to take this opportunity to thank all the lab technicians from Organic Materials Service Laboratory, FACTS Laboratory and Heat Treatment Laboratory for all their assistance in facilitating smooth performance of the experiments. I would like to express my gratitude to my family especially my wife (Ms Vanessa Chong Meng Meng) and friends for showing their support throughout my project and hence, making me believes that the project will be an achievement for me.

Therefore, I would like to grab this opportunity to thank all those who had helped make the project a success.

CHAPTER 1: INTRODUCTION

1. OVERVIEW

1.1 Background

Current research reveal if the world continues with its present rate of development and population growth, global energy consumption is projected to expand by 350% in the year 2100. Few credible options are available to meet that need and among the various proposals, nuclear technology offered attractive potential. If the energy content from known uranium reserves could be efficiently harnessed, it would be 60 times that of the known world oil reserves, 50 times the known gas reserves, 20 times the known coal reserves, 260 times the energy from using only light water reactor technology, or the equivalent of around 90 trillion barrels of oil with values worth \$7.3 quadrillion assuming an oil price equivalent of \$80 per barrel [1-4]. In addition, there will be no emission of carbon related pollutants to the environment by adopting nuclear power as compared to those of harvesting energy from coal. Nevertheless, risk must be considered in the context of assessing the ultimate reward of employing nuclear technology.

Development in nuclear technology should be coupled with improved safety measures to prevent nuclear catastrophes such as those which have occurred in the past, the Chernobyl nuclear reactor meltdown in Ukraine April 26, 1986 and more recently witnessed, release of harmful nuclear radiation near Fukushima Daiichi power plant on March 11, 2011 upon a massive earthquake [2-9]. Radioactive materials are typically identified using a combination of devices, working together, to detect their invisible gamma and neutron radiation emissions depicted in Fig 1 [10]. Gamma rays produced through radioactive decay own the highest energy in the electromagnetic spectrum and

can penetrate most materials even when the radiation source is protected by concrete, dirt, or a few centimeters of lead. However, gamma rays can only be examined indirectly by observing their reactions with detector materials known as scintillators. Scintillation is a technique whereby radiation interacts with a material to produce a brief but measurable flash of light. The precision of the scintillator material's response defines the material ability to differentiate between gamma rays that have similar energies and being able to pick up very weak signal. Such discrimination is essential as not all gamma rays are indicative of a source that poses a threat to the society as some of the signals generated might be due to background interferences.

Reports have indicated that studies on organic single crystal scintillation detectors (fast neutron detectors) have exponentially increased worldwide after the first report on organic crystal electro-/photo-luminescence by Pope et al [10-21]. Organic scintillators have been proposed as the most ideal candidate for fast neutron spectroscopy since they are hydrogen bearing materials. In addition, organic solid scintillators provide stable light yield for a huge range of temperature as compared to inorganic scintillators. Among the solid crystals scintillators, stilbene and anthracene developed from solution method offers the highest light yield 19,552 photons/MeV (Ph/MeV) [22-24]. However, challenges remained in finding suitable approaches to produce large, high quality (free from defects) single crystals suitable for scintillation devices [22, 23, 25, 26]. Impurities within organic crystal scintillator may weaken the fluorescence signal of the device (poor performance) due to light absorption [11, 22, 23, 27, 28]. Therefore, lower cost crystal growth method to develop perfect long range order and high purity organic single crystals having

superior electro-/photo-luminescence characteristics (light yield) comparable to existing organic scintillator is required. The success in finding the suitable crystal growth technique will activate future extensive usage of fast neutron detectors consisting of novel organic crystalline materials.

On the other hand, in term of transistors applications; silicon has been widely applied in the field of microelectronics [29-31]. However, it is commercially more costly to produce, and technically more challenging to fit to large area devices. Furthermore, its production requires high temperature involvement, which is not suitable for the fabrication of cheap devices built on plastic substrates [31-33]. For these reasons, organic based devices have emerged as the key highlights in future generation semiconductors for flexible electronic technology, and they provide the pros factors of being economical and energy efficient production [31, 32, 34-39].

Based on the rising research activities in the field of transistors, examinations on single crystalline organic materials are significant for achieving the optimal performance with desired semiconductor channels of defect less orientated molecules in comparison with those of thin film devices [34, 37, 40, 41]. Single crystalline organic transistors are more reliable for the investigations of intrinsic material properties than polycrystalline thin film gadgets since extrinsic influence of grain boundaries and structure disorder are not present within the material [34, 35, 37, 42, 43]. In addition, studies have indicated that low densities of impurities on the ppm level or below can critically impact the true intrinsic mobility values (by trapping), whenever an excited state is concerned, such as, e.g., a charge carrier [40, 43-46]. Experimental trials have been conducted to enhance

transistor mobility by engaging organic single crystalline materials as the active platform for the channel within the devices. By doing so, investors will be able to predict the market values of such devices in the future since the intrinsic performance of the organic materials can be tested accurately [34, 35]. Therefore, optimized organic single crystals are fundamentals for the exploration of organic electronics applications with their aim of being simple, flexible, and most vital of all cost efficient manufacturing [34, 35, 40, 47].

In recent decades, considerable attention has gone into the preparation and characterization of high purity anthracene crystals, since anthracene is used as a model organic molecular crystal in studies of solid state properties [42, 48, 49]. Anthracene has been identified as one of the organic molecular crystals, which produces note worthy optical and electronic properties. Since the early analysis about anthracene single crystals in 1948, growth techniques involving anthracene single crystals were mainly directed on the physical vapor transport method and solution method [42, 46, 50-53]. In recent years, zone melting method initiated by Pfann in 1952 as tool for material purification had been employed for selected organic materials that consist anthracene [46, 52, 54-57]. As for stilbene crystals, detailed purification studies have not been well established but managed to gain increasing attention due to their optical potential for scintillation devices. This purification method can be adopted only on materials which will not decompose upon melting [43, 56, 57]. In addition, zone melting is efficient for purification if the impurity concentration in the melt vary from the impurity concentration in the solid phase [54-56, 58].

Meanwhile, owing to the complex design of the furnace and the temperature controlling coordination, this powerful method is not easily available to general research and institution laboratories [49, 53, 54]. Since the commercial equipment for growth of organic single crystals from the melt is not readily obtainable, the fabrication of own apparatus and investigations of its functionality is a significant task. The present work is directed to the production of an economical, versatile and simple zone melting furnace for the synthesis of desired quality bulk organic single crystals.

In this study, large size (few centimeters) and high quality selenium (proof of concept) as well as anthracene and trans-stilbene single crystals were grown by versatile zone melting furnace. We have conducted studies on the crystal structure, morphology and purity of selenium as well as those selected organic crystals by adopting Powder X-ray Diffraction (XRD), Energy Dispersive X-Ray analysis (EDX), Laser Desorption Ionization-Time of Flight Mass Spectrometry (LDI-ToF MS), Fourier-Transform Infrared Spectroscopy (FT-IR), Atomic Force Microscopy (AFM), optical microscopy (using polarized light technique) and photoluminescence (light yield). The characterization studies of selenium, anthracene and trans-stilbene ingots synthesized from melt are well in accordance with the standard values. Due to the limited availability of the technology within facility lab, we were not able to evaluate on the scintillation properties of the crystals acquired under excitation from gamma rays. However, we been using the UV excitation energy instead as reference which been proposed as the next alternative in most literatures and indicated that detailed scintillation measurement based on radioactive source should be conducted for future work.

1.2 Motivations

As indicated in most literatures, one of the efficient ways to detect recoil protons produced by fast neutrons during radioactive decay is through the organic scintillators, such as stilbene and anthracene crystals. The energy of the neutron is equivalent to the energy of the recoil proton (transfer of kinetic energy) captured by the scintillation device and this enable mapping of the identity of the radioactive source. In term of operation, the scintillator will generate photons of light in response to incident radiation; following next, a sensitive photomultiplier tube will convert the light to an electrical signal and the photomultiplier tube output will be process by necessary electronics to provide the results as shown in Fig 1 [10, 20, 22, 23, 59].

Although organic single crystal scintillator which includes anthracene and stilbene offer high light yield suitable for fast neutron detection but they are challenging and costly to obtain in large sizes greater than a few centimeters in dimension since they can be subjected to thermal and mechanical shock during synthesis especially when melt growth techniques are involved. In addition, owing to the nature of high vapor pressure for these organic materials, they are volatile and will sublime easily when they experience heat source during the growth, thus leading to formation of smaller crystal dimensions not viable for industrial usage [10, 19, 20, 22, 23, 60, 61]. Currently, most of the growth methods associated with such materials has been limited to low temperature solution growth which is a slow process and suffers from possible contamination through solvent inclusion [11, 22, 23, 26, 27]. Therefore, the studies on melt growth technique and optimization of the growth parameters to produce bulk organic crystals with increased perfection for commercial application are necessary.

Meanwhile, remarkable advancement has been achieved during the last few years in the field of "plastic" electronics. The low charge carrier transport properties that have commonly been linked with organic based materials have been raised by several folds, from measurements on the magnitude of 10^{-5} cm²/Vs to those exceeding 1 cm²/Vs in certain situations [32, 36, 37]. This significant progress has been attained mainly by a random configuration with regards to methodology of organic crystal growth. [32, 37, 38, 62].

Process involving organic crystal synthesis can be mainly divided into three classifications, pending on the medium conditions: development from gas phase, growth from solutions and synthesis from the molten state of the relevant crystal. Among these three general methods, knowledge on the melt growth synthesis is the least acquired as compared to the other two processes [44, 46, 50, 51, 56, 63]. This method consists of crystallization by fusion and re-solidification of the pure component. It has many advantages. The rate of growth, in general, is much higher in this method than that achievable by other methods. Since pure material is used, no impurities are introduced in the growth process except any contamination from the crucible and the surrounding atmosphere [56, 62, 63]. We believe the availability of pure organic single crystal through the melt growth refinement will enable us to identify the intrinsic potential of these materials for both scintillation and electronic devices. Hence, due to these advantages, it is commercially the most important method of crystal growth.

Fig. 1: Scintillation detector mechanism: (a) Overview of the scintillation device & (b) Operation of scintillation crystal [10]

1.3 Objectives

Bulk organic single crystals will generate strong impact on scintillator detectors and micro electronics devices in future. Early commercial development of organics as scintillators for neutron detection as well as active transport materials in light emitting diodes been successful. Despite the fact that organics are able to generate certain market values, the light yield of organic scintillators and physics involving the charge carrier

transport is still unclearly defined and till a large extent, affected by the presence of foreign contaminants, thus impeding the performances of the devices. Up to date, the identification of impurities present within the host organic materials remain challenging and their interference with the optical behavior of the single crystals required more in depth understanding as it has been noted that only light inhibiting contaminants will affect the light yield generated. On the other hand for transistor application, scientists been doubtful if the transport mechanism of organic semiconductors can be consistently elaborated through band theory, similar to those conditions in inorganic semiconductors, or if novel concepts that illustrate the charge carriers as localized entities are essential [36, 37, 41, 45].

Nevertheless, in many organic semiconductors the carrier transport and optical characteristics are critically impacted by the presence of both chemical as well as structural defects. Thus, in order to probe and gain deeper understanding relevant to the physics governing the transport/photoluminescence in this class of materials, one has to inspect samples with low content of structural disorientation and foreign materials; for instance, organic single crystals of low defect concentrations.

This research aims to develop high quality bulk organic single crystal by adopting zone melting technique introduced by Pfann who envisioned the brilliant idea of passing a molten zone along a bar of material so as to refine the impurities based on the factor distribution coefficient k , illustrated as the ratio of the solute concentration in the freezing solid to that in the main content of the liquid shown in Fig. 2 [55-57, 63, 64]. The magnitude of k can be greater or less than unity, depending on whether the solute raises

or reduces, respectively, the melting point of the solvent. Thus, impurities travel along, or opposite to, the zones, pending on whether they reduce or increase the melting point of the charge substance [55-57, 63, 64].

Since the commercial equipment for development of organic crystal from melt is not readily accessible within research laboratory [49, 54], the design of own zone refining furnace (selection of the travel mechanism, heating means, containers and charge shapes) and study on the optimization of the parameters for zone refining operation is required. The various parameters which will affect the quality of the zone refined organic material include firstly, the number of zone passes in the same direction (in practice there is an upper limit to the purity obtainable); secondly, the travel rate (zone speed) of the molten zone (if the travel rate is too high the impurities in the molten zone are again incorporated into the solid phase on solidification before they can diffuse away from the fast moving zone boundary into the inner parts of the zone); thirdly, zone length which should be as small as possible for efficient refinement (varies between one tenth of the sample length); last of all, temperature of the heater should be kept near the melting point of the sample to avoid stresses and deformation of the sample upon cooling [54-57, 63, 65-67].

In order to validate the functionality of the self designed zone melting apparatus, inorganic semiconductor, selenium which has been well established in the field for purification by zone melting technique will be put to test [68, 69]. Upon the successful implementation of the zone refining apparatus, highly cited organic materials with great commercial values, bulk anthracene together with trans-stilbene single crystal will be

produced and tested for purity as well as perfection based on various characterization tools indicated earlier in introduction.

Fig. 2: Growth of crystals by zone melting (1) Quartz tube (2) Heating coils (3) Silica boat (4) Seed (5) Molten zone (6) Polycrystalline bar (7) Inlet and outlet of inert gas [56]

1.4 Novelty

It's been widely accepted that organic semiconductors will be able to effectively contend with inorganic semiconductors for technology that prefer higher mechanical flexibility, high efficiency, portable, large surface area coverage, and economical bulk production. Current successful organic semiconductors devices consist highly efficient scintillation detectors (performance index determined by visible photons emitted per absorbed MeV of x-ray), “electronic” paper, all organic active LED displays, “smart” cards, and organic solar cells (Fig. 3) [11, 24, 32, 36-39, 70]. Nevertheless, the potential of organic semiconductors has not been fully uncovered and among the diverse contributions limiting the device specifications, the purity of the host materials is one of the most critical ones as it directly influences not only the effectiveness but also the dependability of devices [11, 22, 27, 37, 70]. Indeed, the material purity is an imperative matter of apprehension in organic semiconductors because foreign materials extensively impact the optical property/carrier mobilities in organic materials.

Purification method from melt growth (floating zone and zone melting technique) has been well established for inorganic semiconductors such as silicon but rarely studied

for organic semiconductors due to factors which include thermal instability of certain organic materials which decompose upon melting, surface tension of organic melts being too low in value to enable a stable molten zone for floating zone growth under normal gravity, sublimation issue for organic substances with relatively high vapor pressure and the inaccessibility of commercial equipment within research laboratory for growth of organic single crystal [49, 54, 62, 71].

Therefore, the research on development of high quality organic single crystal such as anthracene and trans-stilbene (model material for study of solid state/optical properties due to higher oxidative stability/scintillation pulses) [49, 50] from melt by applying zone refining technique as well as the effectiveness of the self designed zone melting apparatus may prove vital for better understanding of the impacts of impurities on the optical property/electronic of organic semiconductors and to enhance the devices performances of organic semiconductors. In addition, knowledge gained in this study may be applied to explore suitable organic semiconductors (Anthraquinone and Di-phenyl anthracene etc) [58, 66, 72-74] that may zone refined for improved light yield/field effect mobility through the removal of impurities which act as light inhibitors/traps. Meanwhile, the success in the production of huge single crystals of organic materials will enable the creation of organic wafers for improved compatibility with epitaxial growth of organic compounds (those unsuitable for growth from pure melt) through physical vapor transport method. Currently, processes of epitaxial growth of organic semiconductors are studied on silicon wafer or on glass, in spite of expansion coefficient incompatibility

which lead to undesirable result such as formation of cracks within the samples [32, 34, 35, 63]

Fig. 3 (a): Development of Organic vs. Inorganic scintillation devices [24]

Fig. 3 (b): Roadmap for development of organic electronic devices [32]

CHAPTER 2: LITERATURE REVIEW

2. RESEARCH

2.1 Research on Global Impact of Nuclear Technology

Since the accidents in Chernobyl on 26 April 1986 where unit 4 of the nuclear power plant was damaged by two impactful explosions in the core of the its unit 4 reactor leading massive radioactive leakage, few developments have taken place in areas of science, society, politics, and the environment. Firstly, the political climate has changed whereby in the 1980s, during the cold war, nuclear power came to be associated with atomic weapons of massive destruction leading fears and less acceptance among people towards nuclear power stations. However, over the next few years, expansion within the industrializations have resulted in the rise of consumption of energy and humanity turns toward fuel energy harvested from coals, oil and gas related materials but to realize in the alarming harm done towards the environment known as "global warming". Hence, secondly, the need to reduce CO₂ emissions to mitigate climate change contributed to a more positive perception of nuclear power [5, 6, 75-77].

In addition, a third more important factor that seemed to drive favor of nuclear technology was the perceived economic benefits of nuclear power. A country with nuclear power plants can be more independent, has a secure energy supply, and produces relatively cheap and sufficient energy to meet the increasing demand for energy consumption. Based on findings of UK energy statistics, 18 kWh per day per person (44 GW) is directed into industry and at the point of the study, the population density been rounded to 60 million. Therefore, in summary, to decarbonize industry using such way, similar amount of new low carbon electricity produced through alternative means has to

be attained and nuclear energy source been proposed as the promising option [5, 6, 75-77].

All these factors resulted in a more positive public perception about nuclear power globally before the accident in Fukushima on March 11, 2011. Whereas only 49% of the U.S. population favored the use of nuclear power for electricity generation in 1983, this percentage increased to 74% in 2010. Meanwhile, within the 27 European member of states, the number of people supporting the expansion of nuclear power has increased from 14% in 2006 to 17% in 2009. Nevertheless, the world has witnessed the risks involved in the usage of such power but the benefits provided could not be undermine. Hence, continuous efforts been strived towards developments of measures to prevent the occurrence of the nuclear catastrophe. Enhancement in the radiation detection capabilities will be an essential component in international effort to monitor and minimize the extent of damage done during the event of radiation leakage in the early stage of the disaster. In addition, with improved radiation detection systems in place within security borders, proliferation of illicit nuclear weapons could be prevented [5, 7, 75-78].

2.2 Research on Single Crystal Organic Scintillators

The capability to proficiently distinguish low counts of fast neutrons in a mixture of strong gamma ray condition is essential for nuclear detection and for deterrence of illegal nuclear materials activities since fast neutrons are prominent indication of the existence of fissile substance such as Plutonium or Highly-Enriched Uranium [11, 22, 23, 25-27]. Organic scintillators are widely deployed to determine fast neutrons partly owing to their high concentration of hydrogen that enables neutron detection through a process known as proton recoil. Highly active neutrons found in the occurrence of nuclear radiation will strike the target light nucleus in the detector and generate the recoil particles (through transferring of their kinetic energy), which are then identified by the measuring device. The intensity of light yield (optical signal) generated and captured by the detector will enable the identification of the nuclear material involved. This explains the reason why hydrogenous materials are usually recommended as detector of highly energized neutrons since energy shift from active neutrons is more successful for the lightest target nuclei [10, 19, 22, 59, 79, 80]. For these scintillation devices, the differentiation of the neutrons energy over those of gamma rays is achievable with the application of the pulse shape discrimination (PSD), whereby the neutron and the gamma ray reactions of the materials are identified by way of the belated temporal signal distinctiveness of neutrons.

At the moment, only few liquid organic scintillators featuring PSD property are accessible for neutron detection. In addition, liquid scintillators suffer from flammability issues when in contact with air due to their low flash point and toxicity problems which reduced their suitability for application as detectors. Meanwhile, plastic scintillators are

less costly and enable fast timing resolution but they produce low gamma ray energy resolution as well as undesirable gamma ray detection efficacy. Among solid compounds (crystal scintillators), single crystals stilbene and anthracene have been identified as the most effective materials for neutron/gamma ray discrimination. However, challenges remain in growing them to large sizes (above 1 inch) for industrial application due to the macrostructures formations during the synthesis process which affect the light output and scintillation properties.

In recent studies, attentions had been given to development of common hydrocarbons compounds consisting of benzene ring with low atomic number Z constituents and high concentration of hydrogen for scintillation devices. For instance, there are research facilities which are performing production of the organic scintillators in large scales using solution and Bridgman technique but these methods are still within the stage of optimization and hence, they are not commercially available. Among the novel crystals that have been developed by solution method consisting of ammonium salicylate, salicylamide, tetraphenylbutadiene, triphenylbenzene, anthracene, stilbene and diphenylanthracene, which exhibited moderate scintillation light yield (LY) had been achieved successfully as shown in Fig. 4 [11, 22, 23, 25-27].

Nevertheless, an extensive usage of this crystal is limited due to the challenges in suitable growth techniques with minimized defects. For the case of solution growth organic scintillators, solvent inclusions may led to the complication of impurities present within the host materials while the success of the purification by recrystallization will depend on the solubility of the impurity in the applied solvent. In addition, when large

scale production of scintillator is required for commercial application, melt growth technique is more established and cost efficient (less production time) as compared to solution growth method. However, cracks introduced during the heating and cooling of the organic crystal ingot will be an issue during application of melts growth techniques which need to be address (optimization of the thermal gradient). Meanwhile, it has been noted that not all the impurities will affect the light yield generated within the host detectors. Only the light inhibiting contaminants will be having an impact on the sensitivity of the nuclear sensor (scintillator). Thus, studies on the presence of light inhibiting impurities are essential and at the presence rare due to limited availability of pure organic scintillators. Till date, both anthracene and stilbene organic single crystal scintillator have been suggested in the literatures to offer promising optical performance for scintillation field where the scintillation pulses of these crystals are about five folds the amplitude of those from naphthalene which had been claimed to be the first large volume organic scintillator [11, 19, 22, 23, 25-27, 61, 81-83].

Fig. 4: Beta-excited radioluminescence spectra acquired for all the solution grown crystals. Light yields may be compared in an absolute sense [22]

2.3 Research on Single Crystal Organic Field Effect Transistors (SC-OFETs)

Since their discovery in the mid 1980s, organic field effect transistors (OFETs) devices have received much attention due to their possible appliances in large area, economical, flexible and printed electronics [32, 36, 38, 39]. OFETs as shown in Fig. 5 are considered as key building blocks for practical electronic applications [32, 34, 38, 39]. On the scientific side, OFET is also an important object for carrying out investigation on organic electronics and testing novel organic semiconductors. To date, there have been considerable efforts devoted to obtaining satisfactory OFETs and practicable organic circuits, and a large number of novel semiconductors and new fabrication techniques have been devised for improving performances of OFETs especially the charge transport mobility [32, 34, 36, 37].

Due to the limited dimension of polaronic carriers found in the molecular hosts, the active channel in organic based devices extends in the translational path for only few mono layers. Owing to the same argument, polarons interrelate robustly with chemical contaminants and orientation defects. As a consequence the polaronic transport in OFETs is very responsive to the presence of electronic defects which result in carrier trapping and impede the electrical performance of single crystalline field effect transistors [32, 36, 37, 84]. Presence of defects and contaminants impact the electronic states energetically differ from the crystal states. Study on the correlation of band gap states with structural flaws and contaminants are still largely unknown. Formation of undesired flaws in organic based devices often continues as a result of surface oxidation processes and the stress produced by high volume of electric fields in the gadget during operation. These processes resulted in large disparity within device functionality [49, 84, 85].

Meanwhile OFETs based on thin film innovations have established substantial market shares in the past several years. Upon ongoing breakthrough in the research grounds, the room temperature field effect mobility (μ_{FET}) for the most ideal organic thin film transistors obtained $\mu_{\text{FET}} \sim 1.5 \text{ cm}^2/\text{Vs}$, which is equivalent to those of amorphous silicon based transistors. Since transistor device mobility rises with incremental structural order in thin film materials, there is ample support to believe that field effect transistors created on the platform of free standing single crystalline organic specimens offer the best path to manufacture high performance devices applicable for industrial purpose. However, dissimilar to thin film technology, the research on single crystalline organic transistors are still limited and new. Scarce reports on materials such as tetracene, pentacene, and rubrene related field effect transistors have been investigated recently. As of the moment, attractive molecular crystal such as anthracene has yet to be examined for such function. Based on literatures, Anthracene $\text{C}_{14}\text{H}_{10}$ with a band energy gap $E_g \sim 3.9 \text{ eV}$ has internal molecules held by weak van der waals forces, thus it displays rather low melting point ($\sim 217^\circ\text{C}$) and owns the characteristic of being poor electrical conductor. Nevertheless, mobility characteristics obtained from field effect transistor structures involving anthracene single crystals which was recommended as an competent scintillation device since the light yield generated is 5 folds better than naphthalene [28] and owning improved oxidative stability as compared to pentacene [50] could serve as an important research platform for a general knowledge of charge carrier transport mechanism in organic molecular orientated crystals [34, 49, 84, 86].

The progress in synthesis of optimized single crystalline field effect based devices will be essential for relative analysis of various organic materials and, in particular, for determining transport performance of newly grown crystals. Relevant experiments with thin film technology would involve time taxing and costly work on improving the film structure. Although manufacturing of gadgets tuned with large scale operation is based on thin films, the investigations on single crystalline field effect based devices can be view as an imperative function in the material assessment for applications [32, 49, 84]. The technological yield of organic materials might still be below industrial expectation due to the charge trap mechanism found in the channel crystals, therefore the availability of pure SC-OFETs will gain us a new information to unravel the potential of organic electronic gadgets [34, 49, 84].

Fig. 5: Illustration of OFETs structure (cross section and layout view) [32]

2.4 Research on Zone Melting Technique

This technique was first described by Pfann and it is now one of the most useful methods available for the purification of a large number of materials. It is also most useful for the preparation of single crystals, particularly of semiconductors. Single crystals often result when the method is used for purification. The purpose of the zone when the aim is primarily crystal growth is to produce a temperature gradient near the growing solid/liquid interface. It was Pfann who first realized and exploited the potential of such a zone as a distributor of solutes. Since the technique was first described by him, numerous attempts have been made to improve different aspects of the method. The earliest known paper on zone melting was sighted in 1952. During the next 12 years about a thousand significant journals devoted entirely or largely to some aspects of zone melting appeared, and application of the method was cited briefly in many others [55, 56, 63, 68, 69, 71, 87, 88].

The early major application of zone melting was purifying germanium for use in transistors. The technique was soon broadly employed by transistor and diode producers around the world. Nevertheless, zone refining can be applied to many other materials, in fact to any substance that can safely be melted and that demonstrates a difference in impurity concentration between liquid and freezing solid. At present, commercial applications are dominated by the semiconductors. However, quite a few zone refined metals are available in small quantities and commercial use in the field of chemicals is steadily increasing. In time, it is likely that the greatest commercial use of zone melting will be the purification of organic chemicals [55, 56, 63, 68, 69, 87, 89].

The outcomes of zone melting functions can be expressed generally in terms of parameters of two forms: parameters concerning the apparatus, such as zone length, number of passes, travel rate of the heater (zone speed), temperature of the heater; and a factor of the material, namely, the distribution coefficient k , illustrated as the ratio of the solute concentration in the freezing solid to those in the main content of the liquid. A molten zone passing through an ingot displays two liquid solid interfaces which are firstly, a melting interface and secondly, a freezing interface. The zone is able to redistribute foreign contaminants primarily because of what occurs at the freezing boundary. At the melting region, solid material is simply melted and mixed with the contents of the zone. At the freezing boundary, the solutes (impurities) content in the just freezing solid normally varies from those found in the liquid. If the solute reduces the melting point of the solvent, its concentration in the freezing solid will be lesser than in the liquid. Hence solute will be discarded by the freezing solid and accumulate in the liquid providing value of k less than unity as shown in the phase diagram below. Therefore, the impurity with k value less than unity will be carried along in the molten zone. If zone melting is repeated several times in the same direction, the front part of the sample will become more and more pure while the impurities accumulate at the other end [55, 56, 63, 89]. Meanwhile, if the solute increases the melting point of the solvent, its concentration in the freezing region will be higher than in the liquid and the liquid will be exhausted of solute, thus providing k value greater than unity. Hence, a freezing interface can eliminate certain solutes and retain others resulting impurities to be accumulated in one or the other end of the ingot, thereby refining the remainder.

A schematic diagram of the zone melting procedure is shown in Fig. 2. A single crystal seed is placed at one end of a crucible enclosing the substance to be crystallized. The seed is partially melted to obtain a clean surface on which growth can take place, and the zone is then adjusted slowly towards the seed until it is completely wetted. The motion of the zone is then reversed and the seed is allowed to develop. A seed may not be necessary if a material crystallizes readily. In addition, if the left end (tip) of the crucible in Fig. 2 is conical and pointed, it is possible to induce nucleation of a single crystal without a seed (at the beginning only a small amount of the melt is cooled will stimulate the possibility that one crystallite will be formed) . Generally the heat source is radio frequency heating coupled to the melt. Focused radiation from a high intensity lamp or radiative heating from a resistance element have also been employed [43, 56, 63, 68, 89].

The optimum conditions required are a minimum mechanical and thermal fluctuation, a planar melt/crystal interface and a slow growth rate. The crucible material must be compatible with the melt. There might be cases where even if the crucible material is not reactive with the melt, enough wetting of the crucible may occur to allow the grown crystal to stick to its surface. This may cause differential contraction during cooling and thereby strain on the end products. Crucibles made of Pyrex glasses, Vycor, vitreous silica and Quartz have been deemed suitable (non reactive) for materials having melting point less than 1000 °C and they offer the advantage that in a suitably designed furnace, the growth process can be seen [56, 63, 68, 89].

The full impact of the zone melting method upon advances in the field of organic chemistry will probably not be fully realized for some time. The rapid growth of

literature in this area depicts increasing interest and application for this new method. It is emphasized that zone melting and related techniques have potential applications of much broader scope than only purification. Potential uses include separation of azeotropic mixtures, separation of mixtures too heat sensitive to be distilled, and growth of pure single crystals. There are only two basic reasons for the failure of zone melting to purify a crystalline compound. They are firstly, the compound is unstable at or slightly above its melting point and secondly, the starting composition is near that where solid and liquid in equilibrium have the same composition (distribution coefficient is close to unity). Nevertheless, it should never be concluded that zone melting is inapplicable for a particular purification until zone travel rates below 1mm/hr, with at least ten zone passes, are employed [56, 90-92]

[56]

CHAPTER 3: METHODOLOGY ON GROWTH & ANALYSIS OF INORGANIC & ORGANIC COMPOUNDS

3. METHODOLOGY

Inorganic Compound (Proof of Concept)

3.1 Research on Efficiency of HZM Furnace for Se Growth & Purification

3.1.1 OBJECTIVE:

- To investigate the effectiveness of the self designed HZM (horizontal zone melting) furnace for the synthesis of selenium (Se) single crystal and to optimize the operation parameters required to refine the impurities within the precursor

3.1.2 BACKGROUND:

Zone refining was invented by Pfann as a tool for material purification. This purification method can be applied only on materials which will not decompose upon melting. Zone refining is based on the fact that a binary liquid mixture of host material (A) and impurity (B) usually forms crystals of different relative composition upon cooling [21].

$$k_B = \left[\frac{B}{A+B} \right]_{solid} / \left[\frac{B}{A+B} \right]_{liquid} = \frac{C_B^s}{C_B^l} \neq 1 \quad \text{(Equation 1)}$$

As shown in equation 1, C_B^s and C_B^l are the concentration of the impurity amount B in the solid (s) and liquid (l) phases respectively. K_B is the distribution coefficient of the impurity amount B in the binary liquid system. A is the amount of the host material. If $K_B < 1$ then crystallization (or freezing) of the molten phase of a binary liquid in the

ingot would result in a compound purer by a factor of K_B in the beginning compared to the portion which solidifies at later time. On the other hand, for $K_B > 1$, the solidified portion at the later time will have relatively higher purity compared to the portion solidified in the beginning [55-58, 63].

3.1.3 REAGENTS AND EQUIPMENTS:

- Amorphous Selenium (Se) Shots (purity 99%) from Sigma Aldrich
- Self Designed Horizontal Zone Melting (HZM) Furnace
- Ultrasonic Disc Cutter
- D8 Advance Bruker AXS Diffractometer
- Scanning Electron Microscope (JEOL JSM 6360) equipped with EDX
- Leica Optical Microscope

3.1.4 PROCEDURES:

(I) Horizontal Zone Melting (HZM) Process:

Amorphous selenium shots (99% purity) from Sigma Aldrich were used as precursors for crystal growth process. The selenium source material was purified by extensive zone refiner constructed in the research facility as shown in Fig. 6. In order to achieve optimum results by zone refining, the following points are vital: (1) the point of contact between the initial cool down (solidify) material and the melt should remain level, (2) the scale of the molten region is adequately reduced so that the gradient of the contaminants content in the heated zone is minimal and (3) the recommended traveling rate of the heated zone should be relatively slow [43, 56]. For optimization purpose, the length of the molten zone was kept at the minimum (1 cm). The zone heater been

constructed from high resistive super kanthal wire connected to AC variable transformer and the heater is enclosed by two quartz cylinders to avoid heat fluctuation owing to ambient temperature variation. The zone speed was 1 cm/h and the commercial powder of selenium was subjected to 30 zone cycles (cross reference from literature) [55, 56, 63, 67-69, 89, 93]. The starting material, amorphous Se shots was loaded in a glass tube, 7 mm in diameter and 15 cm long as shown in Fig. 11. The zone heater was set at a temperature of 230 °C which is slightly above the melting point of selenium (219 °C) so as to avoid stresses and deformations during cooling [55, 68, 69]. Meanwhile, the growth process was performed in an inert environment through the usage of purified Argon gas. When the crystal growth immediately follows the purification of the material, the achieved purity can be preserved during crystal growth [55, 56, 69, 93].

(II) Characterization of Selenium crystal by XRD:

XRD is a technique of confirming the arrangement of atoms within an analyzed sample, whereby beam of X-rays strike the material and diffracts into many precise paths. The diffraction results that encompass position (angles) and amplitudes of the diffracted beam reveals detailed assay regarding the chemical composition as well as crystallographic structure of natural and fabricated products. Every crystalline material will provide an unique diffraction spectrum and can serve as a distinctive mapping for its identity; the position of the peaks and intensity data are used to evaluate the type of substance by cross referencing them with patterns for over 80000 data entries in the international powder diffraction file (PDF) database, compiled by the International Centre for Diffraction Data (ICDD).

Fig. 6: Illustration of zone melting furnace assembly (a) HZM model, (b) HZM setup, (c) VZM model & (d) VZM setup

In addition, XRD has also been known as a versatile and non destructive technique, thus samples can be re-applied for further analysis by other characterization tools [94].

In term of sample preparation; the zone refined selenium crystal was 8 cm in length and three 3 mm thick slices (Fig. 11) at various locations (front, mid and rear section) along the sample were cut by ultrasonic disc cutter and grinded into fine powder for placement in Bruker Powder XRD sample holder (Fig. 9) for XRD analysis (Fig. 7).

The scan duration lasted for a period of one and a half hour with scan rate of approximately one degree per minute employed. In addition, commercial amorphous selenium shots had been grinded for powder XRD analysis using the same experimental settings.

Fig. 7: Overview of characterization tools (a) D8 Advance Bruker AXS Diffractometer, (b) Scanning Electron Microscope (JEOL JSM 6360) equipped with EDX, (c) Shimadzu (Kratos) Axima TOF², (d) Perkin Elmer FT-IR Spectrometer, (e) Atomic Force Microscope & (f) Shimadzu Fluorescence Spectrophotometer RF-5301 PC (350 nm excitation light from a xenon laser)

(III) Characterization of Selenium crystal by EDX:

EDX analysis represents Energy Dispersive X-ray analysis. The EDX analysis system serves as an integrated function of a scanning electron microscope (SEM). During the test, the analyzed sample been hit with an electron beam emitted from the SEM. The emitted electrons from the device interact with the specimen atoms' electrons, displacing

some of them off in the course. A spot emptied by an evicted inner shell electron is eventually taken over by a higher-energy electron from an outer shell. However, the relocated outer electron deplete some of its energy by producing an X-ray signal during the process of occupying the inner shell position [94].

The sum of energy given off by the shifted electron depends on which shell it is relocating from and which position of the shell it is relocating to. In addition, the atom of every element discharges X-rays with distinctive level of energy during the relocating phase. Thus, by analyzing the level of energy present in the X-rays being discharged by a sample during electron beam interaction, the characteristics of the atom from which the X-ray signal was produced can be recognized [94].

For sample preparation; the different segments (front, mid and rear position) of the zone refined selenium crystal which had been earlier grinded for XRD analysis would be placed on surface of carbon tape affixed to the scanning electron microscope, SEM (JEOL JSM 6360) sample holder for EDX analysis in order to identify the impurities within the various sections of the sample. The experimental settings adopted for EDX analysis include accelerating voltage of 15 kV, working distance 12 mm, spot size 40 and signal mode in secondary electron image (SEI). The illustration of the SEM (JEOL JSM 6360) device is shown in Fig. 7.

Organic Compound (Scintillators Applications)

3.2 Research on Efficiency of HZM/VZM Furnace for $C_{14}H_{10}$ Growth & Purification

3.2.1 OBJECTIVE:

- To investigate the effectiveness of the self designed HZM/VZM (Horizontal & Vertical Zone Melting) furnace for the synthesis of $C_{14}H_{10}$ (anthracene) single crystal and to evaluate the purity/quality of the refined crystal based on optimized operation parameters obtained in section 3.1 (Inorganic Compound)
- Comparison on the efficiency of HZM & VZM furnace in segregating impurities
- Scaling up on the growth of Anthracene crystal for industrial application (7 mm vs 20 mm diameter)

3.2.2 REAGENTS AND EQUIPMENTS:

- Anthracene ($C_{14}H_{10}$) Commercial Powder (purity 98%) from Sigma Aldrich
- Xylene Solution from Sigma Aldrich
- Self Designed Horizontal & Vertical Zone Melting (HZM/VZM) Furnace
- Thread Saw
- D8 Advance Bruker AXS Diffractometer
- Shimadzu (Kratos) Axima TOF² (LDI-ToF MS)
- Perkin Elmer FT-IR Spectrometer
- Leica Optical Microscope
- Atomic Force Microscope
- Shimadzu Fluorescence Spectrophotometer RF-5301 PC

3.2.3 PROCEDURES:

(I) Zone Melting (HZM & VZM) Process:

Anthracene is commercially available in diverse purity grade. The most costly sublimed anthracene has been sold as chemical in few grams with price fetching hundreds of dollars per gram [21]. Therefore it seems cost ineffective for melt growth process where hundreds of grams are required for research purpose while even more quantities attaining to few kilograms are required for detectors production. In addition, even the purest anthracene supplied commercially contains tar impurities which deteriorate the fluorescence of single crystals prepared for scintillation purposes. The exact concentration and types of organic impurity within commercial substances is rarely indicated and only such indication like “sublimed materials” designated on purity of commercial material.

Therefore anthracene ($C_{14}H_{10}$) commercial powders (98% purity) from Sigma Aldrich were used as precursors for the experiments of melt crystal growth. The anthracene source material was purified by a horizontal (HZM) and a vertical zone refiner (VZM) constructed in the laboratory as shown in Fig. 6. The reason for modifying the usage of vertical layout is due to the observation when organic compounds are melted in a horizontal tube; anthracene and impurities with vapor pressure higher than anthracene evaporate very fast from the molten zone, thus reducing the efficiency of the process [21]. This phenomenon was not detected in the case of Selenium purification as Se has low vapor pressure. In order to prevent anthracene evaporation and enabling long time anthracene processing, frequently vertical zone refining or vertical Bridgman

crystallization have been carried out in sealed glass ampoules as suggested in literatures [53, 56, 57, 63, 66, 95-99].

Because in our concept the crystallization should be accompanied by efficient purification, we didn't want to use sealed ampoules and introduced a vertical zone refining (melting) in an open quartz ampoule within an ambient pressure atmosphere of inert gas, argon in our case (Fig. 8) [21]. During the melting process, the evaporation from the molten zone is reduced by the upper part of the ingot that is at temperature below melting zone. However the sealing is not perfect, therefore the small, more volatile molecules, for examples solvents present in commercial materials is still escaping from the molten zone and removed from the ingot. Meanwhile, the heavy impurity molecules within anthracene will be separated to both end of the ingot during the zone refinement.

For optimization purpose, we have adopted the same experimental parameters as those of section 3.1. To simplify the system design, a central tube which serve as the chamber where the crystal growth ampoule been purged by flow of argon was held stationary, while the heater was programmed to travel in the vertical motion causing the movement of the molten zone to travel from the tip of the growth ampoule to the top of the ingot. By the end of 30 zone refinement, Anthracene ingot with smaller diameter of 7 mm and six centimeters length had been successfully grown. In addition, larger diameter anthracene crystal (20 mm in diameter) with length of 10 cm been produced. The front tip of the quartz ampoule had been designed to be narrow so as to promote single crystal nucleation during the growth process. Since all apparatus has been made from quartz, the

melting was observed through the transparent furnace and the heater power required for formation of the molten zone has been adjusted visually.

For anthracene, the zone heater was set at a temperature of 230 °C which is slightly above the melting point of anthracene (218 °C) so as to avoid stresses and cracking during cooling [55]. With the slow flow of argon gas within the quartz chamber, the crystal was prevented from contact with atmosphere and by-products or impurities have been purged out of the quartz chamber. This had effectively reduced the material loss due to anthracene evaporation and has not resulted in small, more volatile impurities accumulation in the crystal growth ampoule. Finally, after the 30 zone cycles, the ingot was removed from the ampoule and both ends of the ingot, with concentrated heavy impurities molecules were removed for impurities analysis, while the middle pure ingot was transferred to a new clean ampoule and subjected to additional 10 zone refining cycles under a slow growth rate of 0.5 cm/h in the same growth furnace, which made the total 40 run of zone refining [21].

(II) Characterization of Anthracene crystal by XRD:

The same principle of XRD as explained earlier had been employed for the analysis of zone refined anthracene crystal. In term of sample preparation; the zone refined anthracene crystal at various positions (front, mid and rear section) along the sample were cut by thread saw soaked with Xylene (due to brittle nature of organic crystal) and grinded into fine powder for placement in Bruker Powder XRD sample holder (Fig. 9) for XRD analysis (Fig. 7). Xylene as a solvent has some advantages: (1) it has low vapor pressure, (2) little toxicity and (3) the molecule is comparatively bulky so

that penetration into most crystal lattices is rather unlikely [57]. The scan duration lasted for a period of 15 minutes with scan rate of approximately six degree per minute employed. Meanwhile, commercial powder of anthracene had been grinded for powder XRD analysis (Fig. 9) using the same experimental settings.

Fig. 8: Illustration of vertical zone refinement process. The vertical arrangement of the zone refiner prevents completely evaporation of volatile anthracene from the molted zone. During the vertical movement of molten zone, the small impurity molecules leaves the ingot, due to evaporation, and the heavy impurity molecules are accumulated at the both ends of the ingot [21].

Fig. 9: Photographs of samples preparation for characterization analysis (a) Powder sample of Se for XRD studies, (b) Powder sample of $C_{14}H_{10}$ (anthracene) commercial powder, (c) Powder sample of zone refined $C_{14}H_{10}$ crystal (Taken from mid zone tube) & (d) Purified $C_{14}H_{10}$ crystal on MALDI sample plate holder

(III) Characterization of Anthracene crystal by Laser Desorption Ionization-Time of Flight Mass Spectrometry (LDI-ToF MS):

LDI – MS is a type of mass spectrometry (evaluation on purity of host material), which forms ions from a sample using laser irradiation (pulsed nitrogen laser, emitting photons at $\lambda = 337$ nm; near UV region). The sample is irradiated with the pulsed laser beam to form an ion ‘plume’. An extraction voltage is then applied and ions are accelerated along the ToF mass analyzer to the detector. The detector records the signal as a current, the voltage of which is amplified to the detector output. Sample analysis without a matrix material (Dihydroxybenzoic acid, DHB commonly used for small molecules and synthetic polymers) and engaging the application of carbon tape to

perform laser desorption ionization mass spectrometry (LDI – MS) would be investigated (eliminate complication that arise with the chemical reaction of the matrix with sample) [100, 101].

For sample preparation; the different sections (front, mid and rear portions) of zone refined anthracene crystal that had been grinded for XRD analysis would be placed on the carbon tape affixed to the MALDI (Matrix Assisted Laser Desorption Ionization) sample plate holder (Fig. 9) for LDI-ToF MS analysis (Fig. 7). A blank carbon tape (Fig. 9) would be tested for presence of any possible contamination and anthracene commercial powder would be subjected to the proposed technique. The firing power of the laser is adjusted to a value of 75 in order to minimize the risk of fragmentation or decomposing the sample.

(IV) Characterization of Anthracene crystal by FT-IR spectral studies:

For infrared spectroscopy, IR radiation is omitted through a material. Some of the IR radiation is taken in by the material, while others are transmitted. The obtained spectrum reveals the molecular interaction which consists of absorption and transmission process, thus establishing the identity of the sample. Infrared spectroscopy has been widely engaged for materials evaluation in the research centre for more than fifty years. An infrared spectrum provides crucial information of a sample based on the absorption peaks which correlate to the frequencies of vibrations between the orientation of the atoms found in the material. Since each varying material is a unique binding of atoms, no two samples with varying content will produce the identical infrared data. Hence, infrared spectroscopy can provide positive classification (qualitative analysis) of every individual

type of material. Meanwhile, the amplitude of the peaks in the spectrum is a direct implication of the concentration of material available [94].

In term of sample preparation; Potassium Bromide (KBr) pelleting technique would be employed. The different segments of the zone refined anthracene crystals (grinded fine powder) are sparsely dispersed in KBr matrix such that the pellet is transparent through much of the mid-infrared (2.5-30 μm). It is crucial for the KBr to be non moist in order to achieve a good pellet and rule out the possibility of absorption bands due to the presence of water in the data generated [94]. If a small quantity of the dry solid anthracene sample (0.1 to 2.0 %) is inserted to the KBr prior to pressing, then a pellet can be formed from which a spectrum of the anthracene crystal can be achieved based on FT-IR spectral studies (Fig. 7) which involve background subtraction of the pure KBr pellet.

In addition, wafers (discs) of anthracene which had been obtained through cutting by thread saw soaked with Xylene would be examined by FT-IR spectral analysis so as to compare the results with those achieved by KBr pelleting technique.

(V) Characterization of Anthracene crystal by AFM:

Atomic force microscopy (AFM) is a method to get images and other details from a broad variety of samples within the range of nanometer resolution. The Atomic Force Microscope was initially introduced to rectify basic limitation of STM which can perform imaging specific to conducting or semiconducting surfaces. AFM operates by scanning a very narrow, sharp probe along the sample surface, cautiously sustaining the force between the probe and surface at low energy. Normally, the probe consists of silicon

cantilever with a pointed integrated tip and the deflection of the cantilever due to forces responding on the tip is sensed by a laser engaged on the rear of the cantilever. The laser is then deflected by the cantilever onto a distant photo detector. The motion of the laser spot on the photo detector provides a significantly overstated measurement of the translation of the probe. This design is known as an ocular lever. The probe is then directed over the analyzed material by a piezoelectric scanner, which can generate extremely accurate actions. The coupling of the sharp tip, the very receptive lever, and the highly accurate motion by the scanner, together with the cautious adjustment of probe-sample forces adopted enable the outstanding performance of AFM [11, 94, 97].

Owing to AFM's adaptability, it has been widely received in a number of research topics involving analyzing almost any types of surface, including polymers, ceramics, composites, glass and biological samples. For our research purpose, purified anthracene wafers have been assigned to surface morphological analysis using AFM. Thin slices ($< 5\text{mm}$) of anthracene single crystal wafer would be developed from the purified ingot (mid section) by using precision wire saw WS-22. Polishing of the anthracene wafer will be done on a Xylene soaked lens tissue on a glass optical flat. Literatures have reported that using Xylene as a solvent, a flatness of a few μm per cm^2 can be achieved for anthracene [57].

(VI) Characterization of Anthracene crystal by Fluorescence Measurement:

Organic scintillators have been widely adopted for analyzing the products of fast neutron activities with the nuclei of an intermediate. The scintillator will exhibit the property of luminescence when activated by nuclear radiation sources. For luminescence

that is emitted on exposure to ultra violet or visible rays is called photo luminescence. When the molecule in the base state S_0 is exposed to light, the kinetic energy of the electrons in the molecule is altered, moving the molecule into the excited state S_1 with a higher energy level (Fig. 10). The excited state, however, soon changes back to the base state as the molecule is deactivated by radiating the energy through heat or light. Since part of the energy of the light absorbed has been lost as vibration or heat energy, the light covers a longer wavelength than the light to which the molecules has originally been exposed (Stokes Law) [15, 16, 20, 61, 94].

A scintillation detector is achieved when a scintillator is attached to an electronic light sensor such as photomultiplier tube (PMT). PMTs take in the light emitted by the scintillator and re emit in the form of electrons through the photoelectric effect. The successive creation of those electrons result in an electrical pulse which can be detected and provide vital information about the particle that originally engaged the scintillator [11, 23, 27, 28].

As indicated by literatures, light output of the organic scintillator play a crucial role in evaluating the efficiency and the resolution of the detector. Factors which may undermine the light yield of the organic scintillator include defects such as impurities within the organic crystals (light absorption by impurities) as well as lack of structural perfection (short range order crystal). Therefore, the prepared anthracene single crystal with high purity (thin slice of anthracene wafer polished with Xylene taken from mid section of the VZM ingot) will be tested for its performance in the field of organic scintillation. Fluorescence/photoluminescence (PL) spectra of the above mentioned

anthracene crystals will be measured at room temperature with the 350 nm excitation light from a xenon laser using a fluorospectrophotometer.

Fig. 10: Principles of Fluorescence [61]

3.3 Research on Efficiency of VZM Furnace for C₁₄H₁₂ Growth & Purification

3.3.1 OBJECTIVE:

- To evaluate the effectiveness of the self designed VZM (Vertical Zone Melting) furnace for the growth of C₁₄H₁₂ (Trans-Stilbene) single crystal and to evaluate the purity/quality of the refined crystal based on optimized operation parameters obtained in section 3.2 (Organic Compound - Anthracene)
- Scaling up on the growth of Trans-Stilbene crystal for industrial application (7 mm vs 20 mm diameter)
- To study on the quality/purity of the Trans-Stilbene crystal developed from VZM furnace against Trans-Stilbene crystal developed from repeated crystallization in Toluene solvent

3.3.2 PROCEDURES:

The same experimental conditions as those described in section 3.2 would be engaged with exception of the following changes: (1) trans-stilbene (C₁₄H₁₂) commercial powders (96% purity) from Sigma Aldrich were selected as precursors for the research of melt crystal growth, (2) zone heater was set at a temperature of 140 °C which is slightly above the melting point of trans-stilbene (125 °C) and (3) only vertical layout zone melting furnace will be adopted for the growth of trans-stilbene crystal (7 mm vs 20 mm diameter ingot).

In order to provide better knowledge on the effectiveness of the self designed VZM furnace in segregating the impurities found in Trans-Stilbene crystal; growth of Trans-Stilbene crystal from solution technique which involved repeated crystallization in Toluene solvent been performed (established from literature). A saturated solution of

trans-stilbene commercial powder in organic solvent, Toluene had been prepared by adding excessive quantity of the trans-stilbene commercial powder in toluene followed by stirring in sealed container at room temperature for a period to attain saturation. After which, the saturated solution been heated to 60 °C within the water bath and then slowly cool to room temperature for a period of one week. The small trans-stilbene crystals obtained upon slow evaporation were taken for impurity analysis. In addition, small crystals which yield excellent quality were being chosen under microscopic inspection as seeds for synthesis of larger crystals whereby the seeds been transferred into another newly prepared saturated solution of trans-stilbene powder in toluene solvent and had been heated 20 °C above the saturation (room) temperature follow by slow cooling over a week. The re-crystallized trans-stilbene crystals were subjected to further impurity characterization.

Meanwhile, same characterization tools as those in section 3.2: Powder X-ray Diffraction (XRD), Laser Desorption Ionization-Time of Flight Mass Spectrometry (LDI-ToF MS), Fourier-Transform Infrared Spectroscopy (FT-IR), Atomic Force Microscope (AFM) and Fluorescence Spectrophotometer would be employed to evaluate the quality of the purified Trans-Stilbene crystals and to determine the crystal structures.

Chapter 4: Characterization Studies on Purity of Selenium (Se)

4. FINDINGS AND DISCUSSIONS

4.1: Research on Efficiency of HZM Furnace for Se Growth & Purification

4.1.1 OBSERVATIONS:

Fig. 11: Photographs of selenium (Se) (a) Amorphous Se shots with purity 99% (8 cm), (b) Horizontal zone refined Se crystal (top view), (c) HZM Se crystal (reverse view) & (d) Optical image of Se crystal prepared by ultrasonic disc cutter (3 mm thick)

Upon 30 zones refinement cycles (around 10 days later), the commercial selenium shots formed large ingot (8 cm) as shown in Fig. 11. The appearance of the Se ingot is reflective on the surface and during melting; the molten zone becomes metallic silver with a mirror finishing. Meanwhile, the tip of the ingot is conical as the molten selenium at the front segment takes the shape of the glass container [56, 63].

4.1.2 RESULTS & DISCUSSIONS:

- a. Comment on the effectiveness of HZM Furnace for synthesis and refinement of the Se crystal based on the adopted operation parameters

Fig. 12: XRD pattern of Se (a) Source with 99% purity, (b) Refined crystal (front, mid & rear section) & (c) Inset of refined Se crystal at 27°

Selenium, Se plays a crucial component as group VI element within the II-VI compound semiconductors. In addition, Se been reported as an indirect gap semiconductor providing outstanding semiconducting and photoelectrical properties. It has a generally low melting point similar to anthracene and purification of Se through zone melting technique had been studied earlier by Tsuzuki as well as Burger et al. Solid selenium mainly emerge in four allotropic structures: trigonal (containing

helical chains), double monoclinic structures (α & β containing Se_8 rings) and lastly amorphous Se consisted of a combination of rings and chains [68, 69, 102].

Based on the XRD analysis, the commercial selenium shots provide an amorphous diffraction pattern with broad peaks (lack of crystallinity) observed between angles 2θ ranging from 20 to 100° (Fig. 12). However, after 30 cycles of horizontal zone refinement (HZM), the samples taken from front, mid and rear segment along the ingot revealed the presence of crystalline (highly ordered) material (Fig. 12) which corresponded to Se hexagonal unit cell with $a = 4.3662 \text{ \AA}$, $c = 4.9536 \text{ \AA}$, and space group P31 (based on data entries taken from ICDD). Meanwhile, at low angle range ($2\theta = 27^\circ$), an additional narrow XRD peak which does not belong to Se had been identified in zone refined Se ingot taken from the front segment (Fig. 12).

The additional XRD peak observed in the front portion of the Se ingot suggests the presence of impurity. Hence, EDX analysis had been executed for the three various portion of the Se ingot. As depicted in Fig. 13, the EDX spectrum of HZM Se samples taken from the mid and rear portion revealed 100 At% selenium (1.379 keV). Meanwhile, 18.98 At% of carbon (0.277 keV) and 81.02 At% of Se (1.379 keV) had been observed in the EDX spectrum of HZM Se sample retrieved from the front segment. An average of five EDX readings had been taken for various sections of the Se ingot and the results revealed that carbon had been detected in the front segment. Meanwhile, the counts (EDX spectrum) of the Se had been higher for the mid and rear (18000) as compared to those taken from the front portion (15000).

In summary, Se single crystal (hexagonal) had been developed and the impurity identified in the front segment belongs to carbon. Since carbon had been detected in the front segment, the distribution coefficient, k of carbon within Se should be greater than unitary according to the zone refining theory as explained earlier [56, 57, 63]. The optimized operations parameters inferred from literatures would be adopted for zone refinement of organic crystal.

Fig. 13: EDX spectrum of HZM Se crystal (a) Front section, (b) Mid portion & (c) Rear segment

Chapter 5: Analysis on Purity & Optical Performance of Anthracene ($C_{14}H_{10}$)

5. FINDINGS AND DISCUSSIONS:

Organic Compound (Scintillators Applications)

5.1: Research on Efficiency of HZM/VZM Furnace for $C_{14}H_{10}$ Growth & Purification

5.1.1 OBSERVATIONS:

Fig. 14: Photographs of HZM/VZM anthracene (a) Commercial $C_{14}H_{10}$ powder with purity 98% (8.5 cm), (b) Horizontal zone refined $C_{14}H_{10}$ crystal, (c) Molten zone of $C_{14}H_{10}$ crystal (1 cm), (d) Vertical zone refined $C_{14}H_{10}$ crystal (7 mm diameter), (e) Vertical zone refined bulk $C_{14}H_{10}$ crystal (30 zone cycles) & (f) Vertical zone refined bulk $C_{14}H_{10}$ crystal (40 zone cycles)

Fig. 15: Photographs of VZM anthracene: (a) Anthracene wafer obtained from vertically zone refined $C_{14}H_{10}$ crystal (diameter 7 mm) (b) Optical image of purified anthracene wafer using polarized light technique

Towards the completion of the 30 zone refinement cycles, the anthracene formed large clear crystals: 3.5 cm (HZM-7 mm diameter), 6 cm (VZM-7 mm diameter) and 10 cm (VZM-20 mm diameter) with appearance similar to those described from other crystal growth techniques [44, 53, 56, 57, 65, 66] as shown in Fig. 14. Dark colored region (suspected to be impurities) extending few millimeters (2-5 mm) was visible at the rear of the zone tube. However, one should note that certain impurities may appear in transparent form as well. The observation that most of the impurities tend to accumulate in the rear of the zone tube could be due to their limited solubility in the host crystal, an impurity compound distributes between the solid phase and the molten phase with the distribution coefficient, $k = C_{\text{solid}} / C_{\text{liquid}}$ less than unity in most cases, and accordingly the impurities travel towards the rear as the molten zone is swept through the ingot of the material to be purified [43, 55, 56]. In later stages of the purification (during additional 10 cycles of refinement for the center of the bulk ingot-20 mm diameter), the amount of the dark colored material was successively reduced as depicted in Fig. 14. Meanwhile, the back sublimation issue of anthracene using the horizontal layout led to the lower yield length

of ingot obtained as compared to those of the vertical layout. For the case of vertical layout, the molten precursor been confined to flow downward due to gravity thus there is limited space for sublimation to occur, while for horizontal zone motion during melting, the surface of the molten zone will provide allowance for side way sublimation (back sublimation) to take place. Hence, this observation was one of the factors which led to the preferred orientation of zone furnace design to be vertical for bulk crystal fabrication.

Optical images of purified anthracene were obtained by polarized light technique to evaluate on the crystal quality using Leica Optical Microscope. The purified anthracene wafers were placed in-between two linear polarizing filters. When the directions of the two linear polarizing filters were perpendicular to each other without the presence of single crystal between them, emission of light signal would be zero as shown in Fig. 16(a). The single crystal placed in-between the two polarizing filter could polarize light in another direction while absorbing certain wavelengths of the visible light as shown in Fig. 16(b). Hence, higher degree of crystallinity within the organic crystal will yield higher uniformity in the appearance (color) of the analyzed crystal. The anthracene wafer (Fig. 15) obtained from mid section of the ingot clearly suggest that high degree of crystallinity for the analyzed samples have been achieved since the tone (color) of the anthracene crystal appear highly uniform. In addition, minimal defects and cracks have been observed on the surfaces of the analyzed samples. The observed cracks have been incurred during the removal of the samples from the glass tube rather than the growth process. Hence, the cracks had been developed around the edge of the prepared wafers.

Fig. 16(a): Mechanism of Polarized Light Technique explaining the dark background in the optical photos under polarized light

Fig. 16(b): Mechanism of Polarized Light Technique explaining the color emitted from the crystals in the optical photos under polarized light. The single crystal diffracts the polarized light at the same time absorbs certain wavelengths of the visible light, giving a color to the crystal as seen from our eyes or the microscope detector.

5.1.2 RESULTS & DISCUSSIONS:

a. Comment on the effectiveness of HZM/VZM Furnace for synthesis and refinement of the $C_{14}H_{10}$ (anthracene) crystal based on XRD Analysis

The powder X-ray diffraction studies were conducted for anthracene commercial powder as well as the purified anthracene crystals developed from horizontal and vertical zone melting (HZM & VZM). Anthracene crystals developed from HZM and VZM revealed monoclinic unit cell with $a = 9.5 \text{ \AA}$, $b = 6.0 \text{ \AA}$, $c = 8.5 \text{ \AA}$, $\beta = 103.6^\circ$, and space group P21/a. The lattice parameters evaluated by powder X-ray diffraction studies of the grown anthracene are in good agreement with the International Centre for Diffraction Data (ICDD) values (Fig. 17-20) [21].

Fig. 17: XRD pattern of HZM anthracene (7 mm diameter): Source with 98% purity & refined crystal (front, mid & rear section). Reference data from ICDD of Anthracene $C_{14}H_{10}$ Monoclinic (00-039-1848)

In addition, strengthening of the planes (peaks) of pure monoclinic anthracene in comparison with the diffraction data of anthracene commercial powder has demonstrated the defect reduction during crystallization in our self designed and constructed horizontal/vertical zone refiner used for our experiment (Fig. 17-20). The detection of diffraction peaks associated with pure monoclinic anthracene is the most prominent within the mid segment of the zone refined ingot [21]. For the case of 30 zone cycles refinement in bulk anthracene 20 mm, additional peak which does not belong to anthracene at low angle (< 10 degree) had been observed for the rear segment of the bulk ingot (Fig. 19). Upon successive refinement of mid part of the ingot by 10 additional zone cycles, the low angle impurity peak had been diminished (Fig. 20). The reason for the absence of this foreign peak in the smaller dimension ingot (7 mm diameter) could be due to low level of contaminants present in the measured material where the sensitivity of the powder XRD equipment is insufficient to detect them.

Fig. 18: XRD pattern of VZM anthracene (7 mm diameter): Source with 98% purity & refined crystal (front, mid & rear section). Reference data from ICDD of Anthracene $C_{14}H_{10}$ Monoclinic (00-039-1848)

Fig. 19: XRD pattern of bulk VZM anthracene (20 mm diameter): Source with purity 98% & refined crystal 30 zone cycles (from front, mid & rear section). Reference data from ICDD of Anthracene $C_{14}H_{10}$ Monoclinic (00-039-1848) [21]

Fig. 20: XRD pattern of bulk VZM anthracene (20 mm diameter): Refined crystal 40 zone cycles (from front, mid & rear section). Reference data from ICDD of Anthracene $C_{14}H_{10}$ Monoclinic (00-039-1848)

b. Comment on the effectiveness of HZM/VZM Furnace for synthesis and refinement of the $C_{14}H_{10}$ (anthracene) crystal based on Mass Spectrometry Analysis

Mass spectrometry analysis had been performed to further verify the purity of the developed anthracene from HZM/VZM furnace. When the sample chamber is set to reach vacuum, possible contamination from low molecular mass organic samples such as anthracene (178 m/z) may arise (Fig. 21) if traces of anthracene have been found on the sample plate. However, the level of contamination is insignificant based on the LDI mass spectrum of blank carbon tape shown in Fig. 21 where the intensity of anthracene being detected is relatively low (intensity = 0.3; 0.02% of main peak detected in purified

anthracene). Hence, the application of carbon tape to provide a platform for the analysis of purity within zone refined anthracene crystals would not affect the readings measured.

By analyzing the normalized mass spectrum data of anthracene commercial powder (Fig. 21), one would notice that impurities such as carbazole ($C_{12}H_9N$) at 167 m/z region and 9, 9'Bianthryl ($C_{28}H_{18}$) near 354 m/z region were present within the source [21]. However, these foreign materials had not been detected within the blank carbon tape which indicates that the contamination was not introduced from the preparation of the sample plate but rather from the samples themselves.

Fig. 21: LDI mass spectrum of (a) Blank carbon tape & (b) Anthracene commercial powder with purity 98% (Impurity Carbazole $C_{12}H_9N$ & 9, 9'Bianthryl $C_{28}H_{18}$ detected)

Anthracene material tends to oxidize which always introduced uncertainty about the presence of oxidized derivatives of these materials as impurities [11, 21, 23, 103]. Some of the commonly cited impurities within anthracene include anthraquinone ($C_{14}H_8O_2$), anthrone ($C_{14}H_{10}O$), fluorene ($C_{13}H_{10}$), 9, 10-dihydroanthracene ($C_{14}H_{12}$), tetracene ($C_{18}H_{12}$), carbazole ($C_{12}H_9N$), and bianthryl ($C_{28}H_{18}$) [21, 44, 52, 53, 56, 66, 103-105]. In addition, challenges remained for the extraction of carbazole from anthracene due to their strong affinity with the host material. However, as shown in Fig. 22-24, upon 30 zone cycles of refinement, both carbazole and 9, 9'Bianthryl impurities had been significantly reduced within the front and mid segment of the purified anthracene ingot. Meanwhile, in the rear section of the HZM/VZM anthracene ingot, the concentration of both impurities have been increased, thus this indicate that the impurities have been successfully isolated to the rear which explains the dark colored region observed within the ingot (Fig. 14). As noted in Fig. 22-24, at high concentrations, most of the impurities segregate efficiently from the solid during normal freezing and this is particularly true for the case of carbazole which form solid solutions with anthracene. In addition, based on Fig 22 and 23, we can clearly observed the surge in the intensity of the impurities detected at the rear zone of VZM anthracene in comparison to those of HZM anthracene crystal for the same dimension ampoule (7 mm diameter). The owning factor could be related to the reduction in the efficiency of HZM to redistribute the impurities since certain contaminants sublimed along the ingot rather than being transported within the molten zone. Hence, the observed improvement in the refinement of impurities using VZM furnace motivated

the application of such device for up version growth of anthracene single crystal (industrial scale organic scintillator).

Fig. 22: LDI mass spectrum of anthracene (7 mm diameter) grown from 30 zone cycles HZM furnace (a) Front, (b) Mid & (c) Rear section (Impurity Carbazole $C_{12}H_9N$ & 9, 9'Bianthryl $C_{28}H_{18}$ detected)

Fig. 23: LDI mass spectrum of anthracene (7 mm diameter) grown from 30 zone cycles VZM furnace (a) Front, (b) Mid & (c) Rear section (Impurity Carbazole $C_{12}H_9N$ & 9, 9'Bianthryl $C_{28}H_{18}$ detected)

Fig. 24: LDI mass spectrum of bulk anthracene (20 mm diameter) grown from 30 zone cycles VZM furnace (a) Anthracene commercial powder with purity 98% (b) Front, (c) Mid & (d) Rear section (Impurity Carbazole $C_{12}H_9N$ & 9, 9'Bianthryl $C_{28}H_{18}$ detected) [21]

Fig. 25: LDI mass spectrum of bulk anthracene (20 mm diameter) grown from 40 zone cycles VZM furnace (a) Front, (b) Mid & (c) Rear section

Meanwhile, for the case of 9, 9'Bianthryl impurities, one would notice that the concentration within the rear segment of the purified ingot (30 zone cycles) had risen extensively as compared to the source material (Fig. 21-24). In addition, upon additional 10 zone cycles of refinement for bulk anthracene (20 mm diameter) after the removal of the impure segment; peaks none other than pure anthracene (178 m/z) have diminished within the ingot at various sections (Fig. 25). Anthracene dimers such as 9, 9'Bianthryl and dihydroanthracene have been recognized as initial reaction products in all pyrolysis studies of anthracene [21, 44, 56, 66, 106, 107]. The initial

reaction had not been well understood and various radical intermediates had been proposed [44, 56, 106-108].

The main reaction occurring in the pyrolysis of polynuclear aromatic compounds involves polymerization. The carbonaceous residues that form on heat treatment of a polynuclear aromatic hydrocarbon are composed largely of oligomers of the starting material [44, 56, 66, 106]. In addition, various dimers from anthracene are possible using the force field based simulations which describe a model's internal degrees of freedom by investigating the potential energy surface due to interactions between bonded atoms and since the 9-position is the most reactive, one might expect a predominance of the 9, 9'-dimer [21, 106]. Hence, during the purification, concentration of impurities such as anthracene dimers had been greatly enhanced and been isolated to the rear segment of the ingot due to its distribution coefficient less than unity.

The detection of dimers in the anthracene commercial and purified samples indicates that dimers and probably larger oligomers as well as polymers form and dissociate during the handling of arenes [21, 109]. These issues need separate consideration as the presence of dimers probably modify the transport properties of organic semiconductors but the physics of such doping remains unclear.

c. Comment on the effectiveness of VZM Furnace for synthesis and refinement of the $C_{14}H_{10}$ (anthracene) crystal based on FT-IR Analysis

Fig. 26: FT-IR spectrum of bulk anthracene (20 mm diameter) grown from VZM furnace upon 30 zone cycles (Mid section)

The FT-IR spectral studies were carried out for the middle segment of the anthracene ingot which had been demonstrated to be pure based on the XRD and mass spectrometry analysis. Based on the test results, for both the KBr pelleting technique and single anthracene wafer sampling method; similar IR spectrums had been achieved. As indicated in Fig. 26 & 27, at the mid portion of the IR data for anthracene developed from our self designed zone melting furnace reveals a distinctive peak attributed to aromatic C–H stretch at 3047 cm^{-1} which emerges very sharp. The sharpness of the peak demonstrates that the hydrogen atoms in the anthracene ring are not exerting any bonding

interaction with molecules. The skeletal vibrations (Carbon Carbon double bond) of the ring could be assigned to peaks 1615, 1500 and 1445 cm^{-1} . The appearance of four adjacent hydrogen atoms is evidenced by the peak at 719 cm^{-1} . Out of plane (Carbon Carbon double bond) could be assigned to peak at 469 cm^{-1} [48, 65]. The spectral data of purified anthracene grown from both our HZM and VZM furnaces are in excellent match with those characteristics peaks found for high quality anthracene crystals developed from solution technique [11, 42, 48, 97] as well as vertical Bridgman method [65, 103, 110] whereby the source was purified by recrystallization in distilled dimethyl sulphoxide and dimethyl formamide.

Fig. 27: FT-IR spectrum of bulk anthracene (20 mm) grown from VZM furnace upon 40 zone cycles (Mid section)

d. Comment on the roughness/surface morphology of the $C_{14}H_{10}$ (Anthracene) wafer derived from VZM bulk ingot (20 mm diameter)

Fig. 28: Atomic force microscopy 3-D diagram of $2 \times 2 \mu m^2$ – z-dimension 100 nm/div (a) Bulk Anthracene crystal surface (mid segment of ingot) upon 30 zone cycles $RMS \approx 2.44$ nm & (b) Bulk Anthracene crystal surface (mid segment of ingot) upon 40 zone cycles $RMS \approx 2.45$ nm

As single crystalline silicon wafer are commonly employed in research facilities for epitaxial film deposition, organic single crystalline wafers for organic epitaxial growth are commercially unavailable. Therefore ingots from high purity and good quality anthracene have been cut perpendicular to the ingot growth direction into wafer. The wafer surfaces have been polished using Xylene and roughness of such wafers has been examined. AFM had been used to evaluate the roughness of the wafers prepared from wire saw. The root mean square (rms) surface roughness of both anthracene samples obtained from the mid segment of the bulk ingot (20 mm diameter) upon 30 as well as 40 zone cycles showed value of 2.44 and 2.45 nm respectively (Fig. 28). The smooth surface of the anthracene wafer obtained from the purified ingot could also serve as an ideal platform for optical measurement to determine the performance of the VZM anthracene in term of scintillation application. There will be less random diffraction of light yield for

the smooth anthracene wafer where improved accuracy of the device capability could be captured [59-61, 75].

e. Comment on the optical performance of the C₁₄H₁₀ (Anthracene) wafer derived from VZM bulk ingot (20 mm diameter)

Fluorescence spectra of the bulk purified anthracene wafers obtained from the mid of ingot (30 & 40 zone cycles) were subjected to 350 nm excitation light from a xenon laser at room temperature. According to most studies, the emission range of anthracene lies in the region 360 to 480 nm, thus the recommended excitation wavelength for anthracene adopted is 350 nm [11, 15, 18, 21, 22, 103, 111, 112]. An intense blue fluorescence appeared from the purified anthracene wafers upon interaction with the xenon source from the fluorospectrophotometer, while weaker blue fluorescence had been emitted for the anthracene commercial powder as shown in Fig. 29.

The fluorescence spectrum for purified anthracene acquire from the mid of the ingot shows emission in the 420-480 nm regions with maximum peak at 446 nm (Fig. 29). In addition, the light yield obtained for anthracene wafer attained through 40 zone cycles revealed higher intensity as compared to those achieved for 30 zone cycles of refinement. Since the roughness of both wafers was similar, the improvement in the light yield could be due to undetectable amount of impurity such as anthracene dimers that were present. In addition, the commercial anthracene powder shows emission in the 410-480 nm regions with maximum peak at 422 nm (Fig. 29). It had been observed that the light yield of commercial anthracene powder was much lower than those obtained from purified crystals at 446 nm and the 422 nm emission peak had not been detected in the purified crystal.

Fig. 29: (a) Fluorescence spectra of Commercial & VZM bulk anthracene crystal (Mid; 30 & 40 cycles); 350 nm excitation light from a Xenon laser at room temperature (b) Anthracene commercial powder & (c) Anthracene wafer taken from mid segment of ingot [21]

This divergence in the fluorescence measurement between commercial and purified anthracene crystals occur as the fluorescence properties of crystalline samples are sensitive to chemical impurities, structural defects and reabsorption of fluorescence. Excitons migrating in the crystal are readily captured by impurities and defects thus resulting fluorescence quenching of the host material [11, 15, 18, 21-23, 81, 103]. Hence the low light yield of commercial anthracene powder at 446 nm is resulted by energy transfer to the unemitted impurities such as carbazole and 9, 9'Bianthryl. These results

clearly demonstrate the principle where usage of light yield inhibitor liberated initial starting precursor is crucial to achieve desired optical quality. For the effect of reabsorption, it occurred as absorption spectra at longer wavelength region overlap with fluorescence spectra at the shorter wavelength region, photons emitted in the bulk of the crystals can be reabsorbed by the crystal. Hence, fluorescence spectra at the shorter wavelength region had been suppressed. In the case of single crystals, emitted photons in the bulk of the crystal could propagate in the crystal due to reflection caused by a large difference in the refractive index between crystal and air [11, 15, 18, 21-23, 81, 103]. As a consequence, the effects of reabsorption become more prominent and emission spectra at shorter wavelength, 422 nm had not been noticed for VZM anthracene single crystal.

Chapter 6: Analysis on Purity & Optical Performance of Trans-Stilbene ($C_{14}H_{12}$)

6. FINDINGS AND DISCUSSIONS:

Organic Compound (Scintillators Applications)

6.1: Research on Efficiency of VZM Furnace for $C_{14}H_{12}$ Growth & Purification

6.1.1 OBSERVATIONS:

Upon 30 zone refinement cycles, large clear crystals of trans-stilbene with length of 6 cm for 7 mm diameter ampoule and 10 cm for bulk ampoule (20 mm diameter) had been developed as shown in Fig. 30. Within the tip of the ampoule, dark colored region which had been suspected to be impurities was accumulated for both 30 & 40 zone refined bulk ingot. The same observation had not occurred for the smaller diameter ingot (7 mm) as shown in Fig. 30 probably due to the limited concentration of impurities within the smaller ampoule. Nevertheless, one should realize that certain contaminants may visually appear in transparent form as well. As for the trans-stilbene crystal developed from the toluene solvent, they appeared small and thin transparent platelets with length of four millimeter as shown in Fig. 31. In addition, the polarized optical image of zone refined stilbene crystal shown high degree of crystallinity being developed (Fig. 30).

Fig. 30: Photographs of VZM trans-stilbene (a) Commercial powder, (b) Vertically zone refined $C_{14}H_{12}$ crystal (diameter 7 mm), (c) Vertically zone refined $C_{14}H_{12}$ bulk crystal (diameter 20 mm), (d) Molten zone of $C_{14}H_{12}$ crystal (1 cm), (e) Stilbene wafer obtained from vertically zone refined $C_{14}H_{12}$ crystal (diameter 7 mm) & (f) Optical image of purified stilbene wafer using polarized light technique

Fig. 31: Photographs of trans-stilbene developed from solution growth (a) Setup of the water bath, (b) Recrystallization of $C_{14}H_{12}$ crystal from toluene solvent in tube, (c) $C_{14}H_{12}$ crystal obtained upon recrystallization

6.1.2 RESULTS & DISCUSSIONS:

a. Comment on the effectiveness of VZM Furnace for synthesis and refinement of the $C_{14}H_{12}$ (trans-stilbene) crystal based on XRD Analysis

The crystal form of trans-stilbene and the arrangement of the molecules in the cell have been examined by Robertson and Woodward (1937) [16, 113, 114]. It crystallizes in the monoclinic configuration consisting of space group C_{2h} (P21/a). The unit cell been attributed to four molecules which are grouped at varying geometries into coupling pairs. Two different unique molecules contribute to the asymmetric unit of the crystal. Based on the powder X-ray diffraction studies, the trans-stilbene crystals developed from both solution and melt revealed monoclinic system with $a = 15.9 \text{ \AA}$, $b = 5.7 \text{ \AA}$, $c = 12.4 \text{ \AA}$, $\beta = 114.0^\circ$, and space group P21/a (Fig. 32-35). The lattice parameters evaluated by powder X-ray diffraction studies of the grown trans-stilbene are in good agreement with the International Centre for Diffraction Data (ICDD) values. Meanwhile, enhancement of the planes (peaks) associated with pure monoclinic trans-stilbene in comparison with the diffraction data of trans-stilbene commercial powder has demonstrated the crystal quality improvement during crystallization in our self assembled vertical zone refiner (VZM) used for our experiment (Fig. 32, 34-35). This applies the same for both the ampoules with varying dimensions (7mm diameter and 20 mm bulk diameter).

In addition, for both 30 and 40 cycles of zone refinement, additional low intensity peaks at low angle with values corresponding to 21 and 26 degree which does not belong to trans-stilbene crystals had been observed (Fig. 34 & 35). This could probably suggest the presence of certain impurity at varying concentration throughout the ingot upon zone refinement which limits the efficiency of zone melting technique for removal of such

impurity. Meanwhile, for the smaller dimension ingot, the presence of the foreign peaks at low angle been noticed only for the rear segment of the ingot (Fig. 32). This could be due to the limitation in the sensitivity of the XRD device to detect the presence of low concentration contaminants within the front and mid segment of the ingot. For the case of trans-stilbene obtained from solution growth, this phenomenon had not appeared, while the preferred directional growth is along the (310) plane with maximum intensity detected as shown in Fig. 33.

Fig. 32: XRD pattern of VZM trans-stilbene: refined crystal 30 zone cycles (obtained from front, mid & rear section). Reference data from ICDD of Trans-Stilbene $C_{14}H_{12}$ Monoclinic (00-007-0532)

Fig. 33: XRD pattern of trans-stilbene: Source with purity 96% & recrystallized crystal from toluene solvent. Reference data from ICDD of Trans-Stilbene $C_{14}H_{12}$ Monoclinic (00-007-0532)

Fig. 34: XRD pattern of VZM bulk trans-stilbene: refined crystal 30 zone cycles (obtained from front, mid & rear section). Reference data from ICDD of Trans-Stilbene $C_{14}H_{12}$ Monoclinic (00-007-0532)

Fig. 35: XRD pattern of VZM bulk trans-stilbene 40 zone cycles (front, mid & rear segments). Reference data from ICDD of Trans-Stilbene $C_{14}H_{12}$ Monoclinic (00-007-0532)

b. Comment on the effectiveness of VZM Furnace for synthesis and refinement of the $C_{14}H_{12}$ (trans-stilbene) crystal based on Mass Spectrometry Analysis

In order to identify the composition of the impurity detected within the trans-stilbene crystal ($C_{14}H_{12}$) upon growth from the melt and solution technique as well as the commercial powder (raw material), mass spectrometry analysis had been performed. As seen in Fig. 36 & 37, prominent traces of impurity peak at molecular mass of 192 m/z had been observed for VZM trans-stilbene crystals obtained from various segments of the ingots. Even for the case of trans-stilbene commercial samples whereby our powder X-ray diffraction analysis did not indicate presence of recognizable impurity peak, the mass spectrometry study revealed the existence of such impurity.

As reported in some literatures, for stilbene samples especially those obtained from Merck and Fluka initial materials, an impurity with retention time exceeding that of

stilbene has been found besides of the usual biphenyl, dibenzyl, benzoin, benzalazine, anthracene, fluorenone, para-terphenyl and cis-stilbene traces [56, 66, 90, 115]. Attempt to identify the impurity using IR spectroscopy and high resolution NMR was unsuccessful as no differences were indicated between the crystal samples studied, most probably owing to the factor that the impurity concentration might be too low for reliable detection. As cited by the studies, the problem was resolved using gas chromatography mass spectrometry where the impurity with molecular mass of 192 m/z was narrow down to two likely compounds which were either 1-methylphenanthrene or 4- methylphenanthrene. More probable is just 1-methylphenanthrene ($C_{15}H_{12}$) which has melting point 123 °C closest to that of trans-stilbene (124 °C) and retention time, RT equivalent to 19.20 min. For trans-stilbene, the retention time is identified as 10 min based on GCMS studies. Meanwhile, additional contaminant (RT = 19.367 min) which falls in the same range of molar mass 192 m/z known as 2-Phenylindene ($C_{15}H_{12}$) had been identified by L. Carman et al. through GC/MS chemical analysis on the solution grown trans-stilbene crystals using toluene solvent [24, 47, 66, 85, 90, 94, 115].

Therefore in our research, the impurity detected within the commercial powder as well as zone refined stilbene crystals obtained from various section of the ingot could belong to both 1-methylphenanthrene ($C_{15}H_{12}$) and 2-Phenylindene ($C_{15}H_{12}$). Since the melting point of 2-Phenylindene (157-161 °C) is higher than those of trans-stilbene; according to the principle of zone refining theory, the distribution coefficient of such impurity within host stilbene should be greater than unity and will not travel along with the molten zone but to remain within the front segment of the ingot which is the

beginning position of zone melting. This could be the reason as to the persistent presence of impurity detected at 192 m/z region (front of the ingot) but at a lower concentration than those of the commercial powder since 2-Phenylindene ($C_{15}H_{12}$) been gathered at the front segment of the ingot based on zone refining principle while majority of the 1-methylphenanthrene been segregated to the rear zone of the ingot as seen in Fig. 36-37.

For the case of 1-methylphenanthrene ($C_{15}H_{12}$), it is logical to assume that 1-methylphenanthrene (192 m/z) forms isomorphic crystals with trans-stilbene which has a molecular mass of 180 m/z in its pure form and the value of distribution coefficient should be close to unity. This could explain, in particular, low efficiency of stilbene purification by zone melting where even upon additional 10 cycles of zone refinement for bulk ampoule, traces of the impurity; 1-methylphenanthrene could be detected within the different section of the VZM trans-stilbene ingot as shown in Fig. 38. Nevertheless, our study has shown that concentration of the 1-methylphenanthrene within the ingot (Fig. 36-37) had been mostly segregated to the rear zone during the initial 30 cycles of zone refinement as compared to those of the commercial trans-stilbene material which suggest that zone refining is indeed a powerful tool for purification of most organic scintillators.

Attempt had been made to purify the trans-stilbene commercial powder by repeated recrystallization from toluene solution. As shown in Fig. 39, the concentration of 1-methylphenanthrene and 2-Phenylindene within trans-stilbene crystal developed from the solution growth was much lower than those of the commercial material and was slightly lower than those obtained from the mid segment of stilbene ingot purified by zone melting upon 30 cycles. However, upon repeated recrystallization, the improvement

in the removal of these contaminants from the stilbene crystal through the toluene solvent was minimal and similar to those achieved upon 40 cycles of zone refinement (Fig. 38 & 39). Hence, this suggest that even for the case of purification from toluene solvent, the persistent impurities, 1-methylphenanthrene and 2-Phenylindene within trans-stilbene could not be completely eliminated but both techniques discussed earlier could minimize the concentration of these impurities to similar level.

According to some studies, stilbene and its analogues undergo many interesting photochemical reactions such as photoisomerisation and intra-molecular rearrangements [116-120]. The two isomers of stilbene, Trans and cis-stilbene are known and photochemical interconversion may be effected by direct irradiation or by irradiation in the presence of a sensitizer. Among the various known process, a particular vital photochemical reaction of stilbene is the photocyclodehydrogenation of cis-stilbene to form phenanthrene. The oxidative photochemical reaction of stilbenes was observed earlier during the examination of stilbene and its photochemical isomerization but the process was not well received until Mallory in 1964 thoroughly reviewed the process. Since then, photochemical reaction involving isomerization of the double bond in stilbene has been broadly investigated [116-120]. From a chemical synthesis perspective, the cis/trans-isomerisation responds instantly under the reaction circumstances in such a path that varying combination of cis- and trans-stilbenes still result in the same end results. Thus, the stilbenes can be employed as isomeric configurations/compositions in the photocyclization reaction, even though uniquely, the cis-isomer is the identified isomer having the possibility undergoing further cyclization. The dihydrophenanthrene created

during the process is not stable and will, unless being trapped, return back to the stilbene. There are also instances of hydrogen-shifts at this phase under nonoxidative requisites. Meanwhile, the dihydrophenanthrene has a tendency to be trapped by oxidation to result in the formation of phenanthrene, or by elimination provide an appropriate substituent in the ortho-location on one of the aromatics [116-120]. Therefore this suggests that the presence of 1-methylphenanthrene (192 m/z) found within the stilbene commercial materials are highly possible owing to the ease in the photochemical reaction of stilbene. Meanwhile, ongoing studies been carried out on the excited state dynamics of 2-phenylindene, a stilbene analogue, and discussion on its implications for the photo-isomerization of stilbenes been of great interest [24]. Nevertheless, these impurities could be reduce through our self built VZM system and provide desirable yield as comparable to those of solution growth technique.

Fig. 36: LDI mass spectrum of trans-stilbene grown from VZM furnace (a) Source, (b) Front, (c) Mid & (d) Rear section using 30 zone cycles (Possible impurities: 1-methylphenanthrene & 2-Phenylindene $C_{15}H_{12}$ detected)

Fig. 37: LDI mass spectrum of bulk trans-stilbene grown from VZM furnace (a) Source, (b) Front, (c) Mid & (d) Rear section using 30 zone cycles (Possible impurities: 1-methylphenanthrene & 2-Phenylindene $C_{15}H_{12}$ detected)

Fig. 38: LDI mass spectrum of bulk trans-stilbene grown from VZM furnace (a) Front, (b) Mid & (c) Rear section using 40 zone cycles

Fig. 39: LDI mass spectrum of trans-stilbene grown from (a) Toluene solvent & (b) Repeated recrystallization from toluene solvent with seed crystal (Possible impurities: 1-methylphenanthrene & 2-Phenylindene $C_{15}H_{12}$ detected)

c. Comment on the effectiveness of VZM Furnace for synthesis and refinement of the $C_{14}H_{12}$ (trans-stilbene) crystal based on FT-IR Analysis

Meanwhile, for the purpose of identifying the functional groups present in VZM trans-stilbene, FT-IR spectral studies were carried out using both the KBr pelleting technique and single crystal wafer. For both the techniques, the IR spectrum results attained does not indicate any differences. The IR spectrum (Fig. 40 and 41) of refined trans-stilbene crystals obtained from the melt revealed sharp peak at 3022 cm^{-1} which is attributed to C–H stretch of the aromatic ring. The ring skeletal vibrations have been noticed at positions 1596 , 1498 and 1448 cm^{-1} along the IR data. The mono substitution

found in the aromatic ring is apparent through peak positions located at 690.5 and 763.8 cm^{-1} . As for the Olifinic C–H deformation, the peak is situated at 960 cm^{-1} . The band assignments of the VZM trans-stilbene crystals are well in accordance with that desirable trans-stilbene developed from Bridgman technique [14, 114].

Fig. 40: FT-IR spectrum of bulk trans-stilbene grown from VZM furnace upon 30 zone cycles (Mid section)

Fig. 41: FT-IR spectrum of bulk trans-stilbene grown from VZM furnace upon 40 zone cycles (Mid section)

d. Comment on the roughness/surface morphology of the $C_{14}H_{12}$ (trans-stilbene) wafer derived from VZM bulk ingot (20 mm diameter)

Following the same explanation earlier, due to the limited availability of organic single crystalline wafers for organic epitaxial growth as compared to those of single crystalline silicon wafer employed in epitaxial film deposition, creation and studies on surface morphology of trans-stilbene wafer is essential. In addition, rough surface/defects may form potential wells-traps-for free excitons causing the loss in light yield. Thus, ingots from the VZM trans-stilbene with desirable quality have been processed into wafer whereby cutting has been performed perpendicular to the ingot growth direction. The wafer surfaces have been polished and roughness of such wafers has been evaluated. AFM had been engaged to measure the roughness of the wafers prepared from wire saw.

The root mean square (rms) surface roughness of both trans-stilbene wafers taken from the mid segment of the bulk ingot upon 30 as well as 40 zone cycles revealed value of 3.11 and 3.16 nm respectively (Fig. 42).

Fig. 42: Atomic force microscopy 3-D diagram of $2 \times 2 \mu\text{m}^2$ – z-dimension 100 nm/div (a) Trans-Stilbene crystal surface (mid segment of ingot) upon 30 zone cycles RMS ≈ 3.11 nm & (b) Trans-Stilbene crystal surface (mid segment of ingot) upon 40 zone cycles RMS ≈ 3.16 nm

e. Comment on the optical performance of the $\text{C}_{14}\text{H}_{12}$ (trans-stilbene) wafer derived from VZM bulk ingot (20 mm diameter)

Fluorescence spectra of the purified anthracene wafers attained from the mid of ingot (30 & 40 zone cycles) were examined under 350 nm excitation light from a xenon laser at room temperature. As shown in Fig. 43, the photoluminescence (PL) emission for the synthesized single crystal of trans-stilbene, one can notice that the highest emission occurs in the range from 360-450 nm. The luminescence spectrum provides three distinctive peaks which are positioned at 370, 380 and 400 nm. The satellite peak at both 370 and 380 nm is generally due to the methyl group bounded at varying locations on the phenyl rings within trans-stilbene, while the peak observed at 400 nm could be attributed

to the level of the twisting activity of the single bond between the phenyl group and the ethylene moiety as suggested in some literatures [15, 22, 23, 103, 113, 114, 121]. In comparison to the PL emission of trans-stilbene commercial materials, the PL intensity achieved for VZM trans-stilbene crystal obtained from mid portion of the ingot improved greatly as seen in Fig. 43. This could be account to the reduction in the impurity such as 1-methylphenanthrene within the trans-stilbene crystal since most reports cited that excitons migrating within crystal are easily captured by contaminants and structural defects thereby resulting in fluorescence reduction of the host material [15, 22, 23, 103, 113, 114, 121, 122]. In addition, as indicated in literatures, for impurities (2-Phenylindene) which had been determined with no light inhibiting effect, they will not result in any deficiency of the optical capability of scintillation sensor [115]. Hence in our research, we have managed to produce trans-stilbene single crystal with a substantially reduced content of light yield inhibiting impurities which further enable the improved scintillation performance within current devices to be realized.

Meanwhile, for the slight peak at 360 nm as detected in the commercial trans-stilbene material which had not appeared for the zone refined crystal could be attributed to reabsorption effect whereby luminescence spectra at the shorter wavelength region overlies with absorption spectra at the longer wavelength region, photons discharged in the bulk of the single crystals can be readily taken in by the crystal. Therefore the emission spectra at the shorter wavelength position are restrained. In addition, the PL intensity for zone refined trans-stilbene crystals obtained upon 30 and 40 zone passes revealed similar values which suggest the limitation of the zone refining process to

completely eliminate the light yield inhibiting impurity (1-methylphenanthrene) found in the crystal. However, the optical performance generated by the trans-stilbene crystal developed from our self assembled VZM furnace yield satisfactory result comparable to optimum trans-stilbene achieved through other means such as solution and Bridgman techniques [15, 22, 23, 103, 113, 114, 121].

In term of further research, we firmly believe that uncovering of the precise nature of the impurities (for instance, isomers of methylphenanthrene) responsible for the loss of the light yield will be vital for the continuous strive to achieve improved scintillation devices. With more accurate detection and interpretation of the light yield inhibiting impurity found in stilbene, we will be able to devise appropriate method to further separate such impurities from the host perhaps through combination of various refining techniques which include sublimation, column chromatography, zone melting and re-crystallization.

Fig. 43: (a) Fluorescence spectra of Commercial & VZM trans-stilbene crystal (Mid; 30 & 40 cycles); 350 nm excitation light from a Xenon laser at room temperature & (b) Trans-Stilbene wafer taken from mid segment of ingot

Chapter 7: Conclusion

As our culture and technology have become more sophisticated and advance, the management of risk on broad basis has emerged more critical and essential than ever before. This is especially true for the case of nuclear power technology where greater efforts been generated to monitor the progress and measures been in place to prevent cases of leakage as well as illegal smuggling of related materials. Therefore various organic scintillators been deployed as detectors for neutrons but some of these detectors are less sensitive to gamma rays which are signals generated in mixed radiation field. Among the different known organic detectors, both anthracene and stilbene crystals have been known for good pulse shape discrimination between neutron and gamma ray events which result in better signal resolution to determine the radioactive material involved based on the intensity of the radiation being captured by the detector. However, the detailed scintillation characteristics of these crystals are not completely understood due to the implications of defects and impurities within the host materials which been rarely analyzed in depth. In addition, challenges in term of the synthesis method where stress and cracking during growth and cooling is commonly encountered for traditional melt growth technique to obtain large volume of single crystals. This technical issue has to be address in order for the potential of large organic scintillators to be realized fully.

Meanwhile, the development of desired quality organic single crystals is also essential for understanding semiconducting mechanisms in molecular configurations as it permits evaluation of intrinsic carrier mobility. In the past, the presence of ultra pure, good grades single crystals of silicon or germanium been crucial for uncovering the

electrical properties of inorganic devices. Likewise, the accessibility of desired quality organic semiconducting crystals is vital for the progress of organic electronics. In addition, wafers of organic materials been seldom produced which could provide great research values for studies on epitaxial growth of organic compound similar to those of inorganic semiconductor epitaxial film deposited on single crystal Si wafer.

In this study, an inexpensive, versatile and simple zone melting furnace had been introduced for the growth of varying dimensions (7 mm and 20 mm diameter) anthracene and trans-stilbene single crystal (VZM: 6-10 cm) with desirable purity. Prior to the growth of these organic crystals; the self designed zone melting apparatus had been subjected to the growth of inorganic semiconductor such as selenium for study on the system functionality. Through the Powder X-ray Diffraction (XRD) and Energy Dispersive X-Ray (EDX) analysis, carbon impurities within the selenium single crystal (8 cm) had been refined effectively based on the optimized operation parameters adopted from references.

Next, the optimal experimental conditions (30 zone cycles, zone speed of 1 cm/h, zone length of 1 cm and temperature of the heater 230 °C) had been applied for the refinement of impurities within anthracene crystals and lower melting temperature of 140 °C been adopted for purification of trans-stilbene materials. Additional 10 zone cycles with lower zone speed of 0.5 cm/h been used to refine the middle segment of the anthracene and trans-stilbene ingots obtained from 30 zone passes. Results derived from optical microscopy, XRD, Laser Desorption Ionization-Time of Flight Mass Spectrometry (LDI-ToF MS) and Fourier-Transform Infrared (FT-IR) Spectroscopy

revealed significance level of impurities (carbazole and 9, 9'Bianthryl) had been detected at the rear zone of the purified anthracene ingot. The findings suggested that the distribution coefficient of these impurities should be less than unity whereby the impurities would travel along the molten zone during zone refinement. In addition, the characterization studies have indicated that VZM furnace is better than HZM furnace in term of purification process since the intensity of impurities (carbazole and 9, 9'Bianthryl) identified at the rear zone is higher in vertical as compared to horizontal layout. Meanwhile, the VZM furnace had resolved the issue of anthracene back sublimation within HZM furnace, thus the yield (dimension) of the anthracene crystal had increased. On the other hand, AFM results revealed desirable roughness range for the anthracene wafers produced and the fluorescence studies indicated the improvements in the light yield generated with the removal of the light inhibiting contaminants within the host materials.

For the case of VZM trans-stilbene single crystal, two persistent impurities known as 1-methylphenanthrene & 2-Phenylindene $C_{15}H_{12}$ had been detected within the source material and the ingots. At the front segment of the zone refined ingot, 2-Phenylindene is present, while 1-methylphenanthrene been distributed along the ingot at varying concentration since the distribution coefficient of this contaminant is close to unity with the host material. Nevertheless, majority of the 1-methylphenanthrene been segregated to the rear zone of the ingot with level of impurities matching with those purified through solution method (re-crystallization using toluene solvent). Meanwhile, based on literatures which reported that 2-Phenylindene does not impact the fluorescence within

stilbene and rather, 1-methylphenanthrene been the light inhibiting impurity, we can observe the higher light yield generated for the mid segment of the stilbene ingot with minimal 1-methylphenanthrene as compared to those of the source.

Nevertheless, the quality of the as grown organic crystals through our self designed vertical zone refining furnace are comparable to those high purity achieved through other means (solution and Bridgman techniques etc) available in the literatures. With the optimized parameters, we can apply this technique for evaluation/creation of more organic materials and uncover their potential in the field of scintillation as well as charge transport mechanism. Continuation efforts in the identification of impurities within host organic materials and approaches to reduce them significantly are essential for the improvement in device performance. Perhaps with the enhanced devices capabilities in place, we can enjoy the benefits of technology and marvel at the industrial revolution which may come along.

8. FUTURE WORK

In the past, critical studies on the impact of defects within the host scintillators due to the presence of impurities been rare due to the limited availability of large desirable quality scintillator produced from a promising approach. Most techniques involved in developing scintillator for research studies been suffering from cracks related issues induced from the heating and cooling especially for those melt grown methods though they been claimed to be the efficient technique for creation of scintillation devices for large scale industrial application as compared to those of solution method as well as the physical vapor transport technique.

The success in the introduction of the self assembled vertical zone refiner in our research studies whereby we been exploring and optimizing the operation parameters of zone melting involved for the current most attractive organic scintillators, Anthracene and Stilbene single crystal due to high device performance yielding from high pulse shape discrimination and scintillation efficiency (high light yield generated) will enable the potential of such materials to be realized for greater industrial application. Nevertheless, as indicated in the introduction, detailed scintillation properties of the crystals (Pulse Shape Discrimination as well as Light Yield) had not been evaluated from emission spectra obtained under gamma rays (alpha & beta) excitation due to the limited access to the radioactive source within our research facility and UV sources as cited in literatures been adopted instead. Thus, one of the key interest for the future work proposed is to send the refined crystals for such measurement and to determine their

scintillation performance upon exposure to radioactive sources (Sr/Y~average beta energy 1 MeV similar to excitation energy produced by gamma rays).

Meanwhile, with the creation of bulk organic ingots as well as wafer from our zone refiner system, various assays been performed to analyze and identify the presence of impurities within the host materials. In addition, we have been establishing the effectiveness of the zone refining technique to isolate and remove the various contaminants. Most importantly, we have shown clearly the co-relation between the impurities and scintillation performance of the host through the fluorescence study (light yield). In our analysis, we have noticed that most organic crystal are highly susceptible to photochemical reaction where the present of light inhibiting contaminant will greatly quench the light yield of the scintillation materials. For the case of Stilbene, neither zone refining nor solution method from Toluene recrystallization could completely remove the light inhibiting impurity, 1-methylphenanthrene. Nevertheless, the light yield generated by our designed refiner provide promising results as compared to those shared in the current research literature.

With our recommended zone refiner, we believe it will not be difficult to adopt them for convenient study on other promising organic crystals cited in literatures and to assess their prospective for scintillation tools in the commercial world. In addition, this technique could also enable creation of pure organic semiconductors for better performance in the electronic transistor devices since trapping by impurities been reduced. Meanwhile, studies on epitaxial growth of organic material on organic substrate instead of non compatible glass or Si substrate is possible via the organic wafer created by our

system. Nevertheless, the mechanism involved in the origin of the impurities within the host materials is still complex. In term of scintillation perspective, our knowledge so far from literatures suggested that introduction of an impurity molecular species into the pure scintillator host reduces the scintillation efficiency by interfering through competitive processes at various stages in the photo absorption and emission sequence. Due to its high mobility, an electron produced by the primary ionization process from neutron radiation is susceptible to capture by an impurity species. Such electron captured competes with ion recombination and thus reduces the light yield and the process been known as quenching. Hence, quenching been normally refer to decline of fluorescence amplitude by another foreign molecule which results some of the excited fluorescers to relax to their ground states without producing photons.

Perhaps, with the available ease in creation of the various organic crystals for scintillation devices, the next major focus should be determining the types of impurities which will affect the scintillation efficiency to greater extent and trace their origins if they cannot be completely removed from known purification technique. By devising stringent conditions to reduce their presence in the source materials could further enhance the capability of the scintillation tools for industrial purposes. We strongly believe that establishment of an accurate library consisting of the intrinsic scintillation (light yield) as well as electronic (mobility) properties of pure organic single crystals is highly attainable with the progression we have garnered within our research study so far and would be of great use for reference in the future.

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10. PUBLICATIONS

1. “Impurities in Zone Refining Anthracene Crystals” – Journal of Crystal Growth
(approved), volume 363, page 61-68; first author (Irvine Hong Huamin), Co-authors:
Dr Tan Ke Jie, Dr Toh Ming Lin, Dr Zhang Keke, Dr Jiang Hui & Prof Christian Kloc
2. “Impurities in Zone Refining Trans-Stilbene Crystals” – Journal of Crystal Research
and Technology (In process); first author (Irvine Hong Huamin), Co-authors: Dr Tan
Ke Jie, Dr Toh Ming Lin, Dr Zhang Keke, Dr Jiang Hui & Prof Christian Kloc
3. Oral conference “Crystal Growth of Selenium & Anthracene from the Melt” –
ICMAT Singapore July 2009
4. Oral conference “Crystal Growth of Organic Compounds from the Melt (Anthracene
& Stilbene)” – 76th Annual Conference of the DPG Berlin March 2012
5. Poster presentation “Crystal Growth of High Quality Anthracene from Melt for
Scintillation Study” – ICMAT Singapore 2011

11. Amendments for Thesis

In today nuclear technology context, measurements of fast neutrons have composed a very significant factor in various applications, such as observing fast neutron fluxes from nuclear reactors, neutron scattering experiments and in border security [2, 5, 6, 75, 79, 80]. The main motivating force for the engagement of nuclear energy derived from the projected increment rate of global energy consumption. Harvest of nuclear energy will potentially meet the demand and the process will not release carbon related pollutants to the atmosphere [4, 123-125]. Technique involving fast neutrons detection depends on the recoil particles measurement [19, 20, 60, 79]. In principle, fast neutrons collide with the target light nucleus in the detector and form the recoil particles through transferring their kinetic energy, while the maximum energy of a recoil proton is equivalent to the energy of the neutron [20, 79, 83, 126]. For the purpose of achieving a sensitive detection method, it is vital to have a large area non hygroscopic detector, which allow fast neutron detection and can discriminate neutron scintillations from background signals such as gamma radiation. A scintillation detector with high content of hydrogen such as those of organic single crystal is the most promising way to design a spectrometer for fast neutrons that fulfils such conditions [19, 60, 83, 126].

The known optimal results in fast neutron spectrometry with real time background discrimination has been derived from Anthracene & Stilbene single crystal [15, 20, 22, 23, 25, 59, 78, 80, 83]. However, both Anthracene and Stilbene single crystals are challenging and costly to obtain in large sizes greater than few centimeters in dimension. Even the most perfect structure molecular organic single crystal has a mosaic structure

when subjected to high temperature growth method [19, 60, 126]. The structure perfectness is obtained by the least root mean square random structure orientation. All these crystals consist of the crystal grains with structure defects on their boundaries. For organic crystals, which are monoclinic systems, the coefficient of thermal expansion is position dependent, thus rapid overcooling results in natural crystal cracking and these macrostructures appearing during the growth process will distort the light output and scintillation properties of the organic detectors [19, 60, 78, 126]. Owing to the difficulties encounter in developing organic single crystal from high temperature growth method whereby the crystals can be subjected to damage from both thermal and mechanical shock, alternative organic scintillators such as plastic and liquid scintillators had been considered for their potential in this field. Plastic scintillators provide roughly 20 percent finer resolution for neutron gamma ray discrimination than liquid scintillators while the solid organic single crystal from melt growth, in turn, is about 20 percent finer in resolution than plastics [20, 78, 79]. In term of production cost, liquid scintillators are considered relatively the cheapest, which can be built in large volumes but the drawbacks include materials being toxic, highly flammable due to their low flash point & lower resolution for neutron gamma ray discrimination [10, 20, 60, 79, 80]. Owing to the findings by researchers that organic single crystal yield as the most efficient scintillator detector, intensive research had been directed to overcome the challenges in growth of Anthracene and Stilbene single crystal for dimensions far greater than few centimeters so that feasibility of industrial application is attainable.

Scintillation single crystal materials can be either grown by melt or vapor phase or solution growth techniques [15, 22, 47, 53, 63, 95-97, 103, 114, 121, 127]. The dimension of the synthesized crystal is limited depending upon the growth vessel and the technique which is employed. Synthesis of some organic molecular crystals from the vapor phase results in tiny crystals formation with the disadvantage of large time consumption, while the possibility of solvent occlusion and the solubility limit the growth of crystals from solution method [14, 121]. Therefore, when large volumes of single crystal materials are required for certain applications, melt growth technique may offer viable scaling up processes with better cost effectiveness. As noted by most research, heat transfer in melt growth configuration tend to be complex, and during the cooling cycle the temperature variations inside the ampoule are generating the defects and structural boundaries which will impede the light output generated for scintillation measurement [12, 56, 57, 61, 66, 67, 114, 128]. In addition, based on various literatures, it had been emphasized that some chemical impurities form very efficient traps, such that the crystal fluorescence is dominated by the emission from the guest molecules even at low concentrations as compared to the host material [10, 15, 16, 21, 22, 57, 85, 88, 122, 129]. Hence, the efficiency of proposed Anthracene and Stilbene scintillators rely critically on the crystal quality in term of defects and impurities within the host materials.

Among the various melt growth technique, zone melting technique had been proposed in this study for the growth of potential scintillator organic single crystal since this technique had been considered to be the most generally applicable and efficient way of removing impurities within the host material. Complications faced by most melt

growth technique which involve organic samples include high vapor pressure which result fast evaporation of the materials leading to yield loss; surface tension of organic melts being too low to keep a stable material in the case of floating zone; concerns on the compatibility of crucible to avoid undesired reaction with the melt been resolved with careful preparation of the zone melting setup [56, 87, 90, 91]. Details on the zone melting theory been widely covered by Norbert Karl & William G. Pfann et.al but the assembly of ideal zone melting furnace is still subjected to intensive research as modification been required due to the different thermodynamic nature of materials.

For the purification process in zone melting method, the redistribution of impurities occurs at the freezing interface, while the melting interface continually adds liquid to the zone. The segregation phenomenon at the freezing interface is usually described as a solubility difference of impurities (solutes) in the liquid and solid phases. If part of the impurity remains with the solid phase as the interface moves into the liquid melts, a distribution coefficient, k arises. This coefficient relates the concentration of solute in the solid to that of the liquid at the interface as shown in equation 1 [56, 66, 87, 90].

$$k_B = \left[\frac{B}{A+B} \right]_{solid} / \left[\frac{B}{A+B} \right]_{liquid} = \frac{c_B^s}{c_B^l} \neq 1$$

(Equation 1)

For simplicity, distribution coefficient k been expressed in term of a solute present in small concentration in the liquid and solid phases of a solvent. However, the distribution coefficient can be regard in a much broader aspect encompassing phase

diagram. Illustration depicting the solute decreases the melting point of the solvent in a binary system is shown in Fig 1(a).

Fig 1: Portions of constitutional diagrams in which the freezing point of the solvent is (a) lowered, (b) raised, by the solute [56]

A solution having concentration C_L of solute will be entirely liquid at temperatures above the upper curve, or liquidus region (melting). When the solution is cooled slowly to temperature T during the freezing of the zone melt while the zone heater is directed away, the first solid to appear will be a crystal of solvent containing concentration C_S of solute in solid solution. Do note C_S will be determined by the intersection of the temperature horizontal with the lower curve, or solidus. The equilibrium distribution coefficient k is the ratio C_S/C_L as explained earlier in equation 1. In Fig 1(a), k is less than unity as the liquidus and solidus slope downward. In situation whereby the solute raises the melting point of the solvent where k is greater than unity, the liquidus and solidus will slope upward as shown in Fig 1(b). Hence upon successive

zone cycle translations, the impurities would be accumulated either at the front or rear of the ingot depending on the distribution coefficient greater or less than unity respectively. There are two basic factors which may lead to failure of zone melting to purify a crystalline compound. Firstly, the compound is unstable at or slightly above its melting point and secondly, the starting composition is near that where solid and liquid in equilibrium have the same composition (the eutectic composition) where k is close to unitary value ($K \approx 1$) [56, 66, 90, 91, 96].

The simplest approach to determine the values of the distribution coefficient of the solute in a binary solute solvent system is to consult a phase diagram coupled with knowledge of the growth conditions. If only the solidus concentration or liquidus concentration of the solute at a given temperature is established, the distribution coefficient, k can be estimated by simplified zone refining mathematics as shown in equation 1 coupled with few conditions. The assumptions include (1) the distribution coefficient is constant and independent of all other impurities (then it is possible to do the calculation for one impurity); (2) Diffusion of the impurity in the solid phase can be neglected; (3) The zone has constant width and constant cross-section; (4) Macroscopic zone travel velocity and microscopic crystallization velocities are constant; (5) Melt and solid have the same specific density, independent of temperature; (6) No new impurities are created by isomerisation or decomposition during zone refining. Till date, due to the complexity involved in the zone refining system, researchers have been actively investigating the appropriate thermodynamic relationships involving distribution coefficients of solute beyond ideal solutions. Despite the difficulties encountered, it is crucial to establish a

library of data which indicates the distribution coefficient of the various impurity solute within the potential host material for scintillation detector application as shown in Fig 2.

System host (guest)	k/f [mm h ⁻¹] without stirring	with stirring
naphthalene (β -naphthol)	2.3 / 1.85/	—
fluorene (anthracene)	1.13/0.65	1.33 /9
phenanthrene (anthracene)	—	1.6 /
2,3-dimethylnaphthalene (anthracene)	2.1	—
2,3-dimethylanthracene (tetracene)	> 1	—
dibenzofuran (anthracene)	1.1–1.3	—
brasan ^a (tetracene)	> 1	—
p-terphenyl (tetracene)	> 1	—
naphthalene (anthracene)	0.01 /7	—
carbazole (anthracene)	—	0.5 /5
anthracene (tetracene)	0.10 /1 0.05 /1	0.05 /4
anthracene (anthraquinone)	0.02 /1	0.006/4
anthracene (fluorene)	0.2 /1	—
anthracene (phenanthrene)	0.1 /1	—
anthracene (carbazole)	0.9 /1	0.84 /
anthracene (acridine)	—	0.14 /0.25
anthracene (phenazine)	0.1 /1–10	0.1 /1–10
anthracene (azobenzene)	0.04 /10	—
phenanthrene (fluorene)	—	0.95 /
phenanthrene (dibenzothiophene)	—	0.8 /
phenanthrene (dihydrophenanthrene)	—	0.8 /
	k	χ^b
cyclododecane (acenaphthene)	0.08	0.26
cyclododecane (naphthalene)	0.01	0.39
cyclododecane (perylene)	$2 \cdot 10^{-3}$	0.49
cyclododecane (anthracene)	$3 \cdot 10^{-5}$	0.74
cyclododecane (chrysene)	$2 \cdot 10^{-6}$	0.92

Fig 2: A collection of effective distribution coefficients [57]

By generating such data, one will be able to plan zone refining experiments to remove undesired impurities along the grown ingot which will quench the light yield of scintillator detector, thus reducing the efficacy of the detector. Even more importantly,

understand the limitations/potential of zone melting method for various organic crystal growth which can be apply for broader research beyond scintillation that may include organic electronics devices.

Based on the rationale listed earlier, the design of self assembled zone refining apparatus and optimization of its operation parameters is a significant task. The present work is directed to the fabrication of an inexpensive, versatile and simple zone melting furnace for the study on growth of high quality bulk Anthracene/Stilbene single crystal from small amount of melt. The proposed raw materials were purified by a vertical zone refiner (VZM) constructed in the laboratory as shown in Fig. 3.

Fig. 3: Illustration of zone melting furnace assembly & the refinement process

(Anthracene ($C_{14}H_{10}$) sample) [21]

To prevent organic materials evaporation and enabling longer duration processing, normally vertical zone refining or vertical Bridgman crystallization have been carried out in sealed glass ampoules. However, we adopted a vertical zone refining (melting) in an open glass (quartz) ampoule within an ambient pressure atmosphere of inert gas using pure argon instead of sealed ampoules since we believe crystallization should be accompanied by efficient purification. During the melting process, the evaporation from the molten region is reduced by the upper part of the ingot that is at temperature below the melting zone. Nevertheless the sealing is not perfect, therefore the more volatile small molecules, for examples solvents present in commercial materials is still escaping from the molten zone and removed from the ingot, while the heavy impurities molecules within host (Anthracene/Trans-Stilbene) would be segregated at both ends of the ingot [21].

As illustrated in most reports, optimum operating conditions in zone melting are those which provide the greatest purification possible in a given length of time. Therefore, upon repeated optimization studies, the length of the molten zone was kept at the minimum (1 cm). The zone heater consisted of resistive super kanthal wire connected to AC variable transformer and the heater is enclosed by two quartz cylinders to prevent heat fluctuation due to ambient temperature variation. To simplify the system design, a central tube which serve as the chamber where the crystal growth ampoule been purged by flow of argon was held stationary, while the heater was programmed to travel in the

vertical motion causing the movement of the molten zone to travel from the tip of the growth ampoule to the top of the ingot. By translating the motion of the heater rather than the ampoule, we believe the mechanical vibration within the molten zone interface is minimized significantly so that during the freezing, crystallization can occur slowly with reduced defects formation. The zone speed was 1 cm/h and the commercial powder of samples were subjected to 30 zone cycles.

By adopting the above refinement parameters, organic crystal ingot with smaller diameter of 7 mm and seven centimeters length had been successfully developed as proof of concept to the functionality of the self designed zone refiner system. Meanwhile, larger dimension Anthracene/Trans-Stilbene crystal, 20 mm in diameter with one end sealed and ten centimeters length had been successfully synthesized to demonstrate that scaling of the crystal growth based on the self assembled refiner is attainable. The front tip of the quartz ampoule had been designed to be narrow so as to promote single crystal nucleation during the growth process. Since all apparatus has been made from quartz, the melting was observed through the transparent furnace and the heater power required for formation of the molten zone has been adjusted visually. For the samples, the zone heater was set at a temperature of which is slightly above the melting point of the samples (+ 15 degree Celsius) so as to avoid stresses and deformations during cooling. In addition, the growth process was carried out in an inert environment using purified Argon gas. With the slow convection of argon gas within the quartz chamber, the crystal was kept out from any reaction with atmosphere and impurities have been purged out of the quartz chamber. This had effectively minimized the material loss due to Anthracene/Trans-

Stilbene evaporation and has prevented small, more volatile impurities accumulation within the crystal growth ampoule.

In addition, evaluation on the purity and quality of Anthracene/Stilbene crystal upon zone refinement will be based on utilization of the following analytical tools. The tools include Powder X-ray Diffraction (XRD), Laser Desorption Ionization-Time of Flight Mass Spectrometry (LDI-ToF MS), Fourier-Transform Infrared Spectroscopy (FT-IR), Atomic Force Microscopy (AFM) and Fluorescence Measurement.

As mentioned earlier, both smaller dimension (7mm) ingot and larger dimension ingot (20 mm) had been achieved based on the self designed zone melting furnace with optimized parameters/conditions shared. In addition, as a proof of concept, the growth of selenium ingot and evaluation on the purity been done. Meanwhile, comparison between the horizontal and vertical zone melting setup been established in term of efficiency for the growth and purification of the proposed organic sample such as Anthracene crystal used in the field of scintillation. Owing to back sublimation issue based on design of the horizontal zone refiner, vertical zone refiner been concluded to yield more benefits in term of purification process.

In term of purification, for the case of Anthracene grown sample; 3 segments been evaluated using the Powder X-Ray Diffraction (XRD) technique coupled with mass spectrometry analysis [Laser Desorption Ionization-Time of Flight Mass Spectrometry (LDI-ToF MS)]. By referring to Fig 3 as shown earlier, the 3 segments of the ingot being studied could be classified as Zone A - Tip of the ingot (front segment where heater start to move and molten zone began to travel vertically upward; Zone B - Mid of the ingot;

Zone C - Rear Zone of the ingot which appear as dark colored materials of 3-5 mm. In term of XRD pattern observed, beside stronger signal of peaks detected belonging to Anthracene Monoclinic system as verified by Pawley Refinement method, there are no prominent signs of impurities peak detected within the smaller dimensions (7mm diameter crystals) probably due to the low sensitivity of the device on measuring samples with low counts of impurities. However, for the bulk wafer (20 mm) developed from the 30 zone cycles refinement, additional peak which does not belong to Anthracene at low angle (< 10 degree) had been observed for the rear segment of the bulk ingot at Zone C.

Confirmation on the presence of the impurities detected within the Anthracene commercial source (raw material) been established by measurements using the mass spectrometry analysis. Even for those smaller dimension Anthracene crystals grown where XRD method fail to clearly register the contaminants, the normalized LDI mass spectrum managed to capture the intensity of the foreign materials none other than Anthracene. Distinct mass peaks which belong to Carbazole ($C_{12}H_9N$) at 167 m/z region and 9, 9'Bianthryl ($C_{28}H_{18}$) near 354 m/z region were present within the source as well as Zone C (rear end) of the zone refined ingot. Based on Zone refining theory as discussed, the distribution coefficient of such impurities should be less than one whereby the impurity solute lower the melting point of the solvent and during freezing, they been rejected from the host and travel along the molten zone to be accumulated at the rear zone [55, 56, 67, 96, 98, 103, 106, 107]. However, the determination of the exact value of the distribution could be tricky especially for the case of the 9, 9'Bianthryl which appear as dimers due to thermal reactions which involves polymerization (internal deficiency) [57,

91, 106, 107]. Nevertheless, the results gathered have indicated clearly that upon additional refinement of 10 cycles using our zone refining system with slower growth rate of 5mm/h can help to reduce both the Carbazole ($C_{12}H_9N$) at 167 m/z region and 9, 9'Bianthryl near 354 m/z region at Zone C (rear zone) to a minimal detection level close to zero (reduction of 8% & 18% of the Carbazole and Bianthryl impurities respectively as compared to the 30 cycles of zone refining); refer to Fig 4 and 5.

Fig. 4: LDI mass spectrum of bulk anthracene (20 mm diameter) grown from 30 zone cycles VZM furnace (a) Anthracene commercial powder with purity 98% (b) Front, (c) Mid & (d) Rear section (Impurity Carbazole $C_{12}H_9N$ & 9, 9'Bianthryl $C_{28}H_{18}$ detected) [21]

Fig. 5: LDI mass spectrum of bulk anthracene (20 mm diameter) grown from 40 zone cycles VZM furnace (a) Front, (b) Mid & (c) Rear section

Meanwhile, the Atomic force microscopy (AFM) together with the Infra Red analysis (FTIR) reinforce the quality of the Anthracene wafer developed. More importantly, for the Mid zone of the wafer developed which results clearly revealed as the purest segment, we have obtained the fluorescence spectra (Fig. 6) comparable to those cited Anthracene crystals obtained by other means such as solution growth; refer to Fig 7 in the report. Do note that the excitation wavelength for the cited literature on solution growth Anthracene crystal is based on higher energy (Beta-excited radioluminescence spectra), while the source in our research is based on 350 nm excitation light from a xenon laser (lower energy) at room temperature. The commercial source fluorescence signal been measured and the values attained are much lower, while those of the 40 cycles refined crystals yield the highest output without the presence of

impurities such as Anthracene dimers which quench the light emission from the host material; refer to Fig 6 in the report. Detailed scintillation properties of the crystals (Pulse Shape Discrimination) had not been evaluated from emission spectra obtained under gamma rays (alpha & beta) excitation due to the limited access to the radioactive source within our research facility and ultra violet (UV) sources as cited in literatures been adopted as the next viable alternative.

Fig. 6: (a) Fluorescence spectra of Commercial & VZM bulk anthracene crystal (Mid; 30 & 40 cycles); 350 nm excitation light from a Xenon laser at room temperature (b) Anthracene commercial powder & (c) Anthracene wafer taken from mid segment of ingot [21]

Fig. 7: Beta-excited radioluminescence spectra acquired for all the solution grown crystals. Light yields may be compared in an absolute sense [22]

Upon gaining success in the development of the bulk pure Anthracene single crystal based on the self designed zone refiner, similar approach been adopted for the refinement of the next potential organic scintillator material which is Trans-Stilbene crystal as shown in Fig 8. Three areas of analysis interest along the purified ingot been identified which consisted of Zone A - Tip of the ingot which was the start point of the purification; Zone B - Mid of the ingot (labeled as the purest by most literatures) and Zone C - Rear segment of the ingot. After 30 cycles of refinement, dark colored region of particles accumulated at the tip of the ingot for bulk ampoule (20 mm diameter) as observed visually. Nevertheless, as explained in the thesis, impurities within the host crystal can appear colorless as indicated in some research.

Fig. 8: Illustration of zone refinement process for Trans-Stilbene ($C_{14}H_{12}$) material

Based on Powder X Ray Diffraction studies for both 30 and 40 cycles of zone refinement for bulk Trans-Stilbene material, additional low intensity peaks at low angle with values corresponding to 21 and 26 degree which does not belong to Trans-Stilbene crystals had been observed at Zone A, B & C. This could probably relate the presence of certain foreign materials at varying amount throughout the ingot upon zone purification which limits the efficacy of the zone refinement system whereby the distribution coefficient of such impurity within the host is close to unity (solute has insignificant ability to alter the solvent melting point in the binary phase system). For the case of

Trans-Stilbene obtained from solution growth (alternative approach to test the purity level and benchmark with those results obtained by our self assemble refiner) [82, 115], this phenomenon had not appeared, while the preferred directional growth is along the (310) plane. Failure to detect the foreign peaks could be due to lack of sensitivity for the Powder XRD instrument to detect the low concentration of the impurities.

Adopting a more suitable measuring approach, mass spectroscopy analysis, the impurities identified along Zone A (tip of ingot) are firstly, 1-methylphenanthrene ($C_{15}H_{12}$) which has melting point 123 °C closest to that of Trans-Stilbene (124 °C) and retention time, RT equivalent to 19.20 min and secondly, 2-Phenylindene ($C_{15}H_{12}$) having RT = 19.367 min, melting point 157-161 °C which is higher than those of Trans-Stilbene (Melting point - 124 °C, RT = 10 min). Both the impurities fell in the same range of molar mass 192 m/z, while the molar mass of Trans-Stilbene is revealed as 180 m/z; refer to Fig 9. The identification been re-affirmed by those findings shared by L. Carman et al. through GC/MS chemical analysis on the solution grown trans-stilbene crystals using toluene solvent [24, 47, 66, 85, 90, 94, 115].

In Zone B (Mid of ingot) and Zone C (Rear of the ingot), the impurities identified should belong to 1-methylphenanthrene ($C_{15}H_{12}$). According to the principle of zone refining theory, the distribution coefficient of 2-Phenylindene ($C_{15}H_{12}$) impurity within host stilbene should be greater than unity based on the higher melting point derived and will not travel along with the molten zone but to remain within the front segment of the ingot which is the beginning position of zone melting [56, 57]. This could correlate as to the persistent presence of impurity detected at 192 m/z region (front of the ingot) but at a

lower concentration (20%) than those of the commercial powder since 2-Phenylindene ($C_{15}H_{12}$) been gathered at the front segment of the ingot based on zone refining principle while majority of the 1-methylphenanthrene (melting point slightly lower than host, distribution coefficient close to unity) been segregated to the rear zone of the ingot as seen in Fig. 9.

Fig. 9: LDI mass spectrum of bulk trans-stilbene grown from VZM furnace (a) Source, (b) Front, (c) Mid & (d) Rear section using 30 zone cycles (Possible impurities: 1-methylphenanthrene & 2-Phenylindene $C_{15}H_{12}$ detected)

In order to test the limit of the self designed system to achieve the highest possible purity level for Trans-Stilbene crystal, growth conditions which include 10 progressive cycles of zone purification based on slower zone rate 5 mm/h been adopted

for those Trans-Stilbene materials obtained from Zone B (Mid of ingot - Purest in the 30 cycles of zone refinement). As shown in Fig 10, the most ideal purity level achieved is reduction of the 1-methylphenanthrene ($C_{15}H_{12}$) impurity to 18% in zone B as compared to those achieved in 30 cycles of zone refinement (30%). Even by adopting the solution growth technique as recommended in literature [22, 82, 115], the lowest methylphenanthrene ($C_{15}H_{12}$) impurity level achieved is close to 18%; refer to Fig 11 [24, 47, 66, 85, 90, 94, 115]. This indicates that our self designed system is able to replicate the pure quality Trans-Stilbene crystal despite limitation in the complete removal of the impurities from host material due to distribution coefficient of impurity close to unity of the host crystal. Meanwhile, the origin of the impurities based on cross reference from literatures been associated with the photosensitivity of stilbene whereby Stilbene and its analogues undergo many interesting photochemical reactions such as photoisomerisation and intra-molecular rearrangements [116-120]. Care should be given to minimize such photochemical reaction which will impede the light yield and scintillation performance of the Trans-Stilbene crystal.

Fig. 10: LDI mass spectrum of bulk trans-stilbene grown from VZM furnace (a) Front, (b) Mid & (c) Rear section using 40 zone cycles

Fig. 11: LDI mass spectrum of trans-stilbene grown from (a) Toluene solvent & (b) Repeated recrystallization from toluene solvent with seed crystal (Possible impurities: 1-methylphenanthrene & 2-Phenylindene $C_{15}H_{12}$ detected)

With knowledge gained in the impurities identified in the grown Tran-Stilbene material and conditions to minimize the impurities based on zone refining theory, fluorescence studies been included to analyze the possibility of using the zone refined Trans-Stilbene wafer for scintillator device (light yield performance). As seen in Fig 12, our results show promising fluorescence data comparable to those achieved by Bridgman method; Fig 13. In addition, as indicated in literatures, for impurities (2-Phenylindene) which had been determined with no light inhibiting effect, they will not result in any deficiency of the optical capability of scintillation sensor [115]. Hence in our research,

we have managed to produce trans-stilbene single crystal with a substantially reduced content of light yield inhibiting impurities (1-methylphenanthrene) which further enable the improved scintillation performance within current devices to be realized.

Fig. 12: (a) Fluorescence spectra of Commercial & VZM trans-stilbene crystal (Mid; 30 & 40 cycles); 350 nm excitation light from a Xenon laser at room temperature & (b) Trans-Stilbene wafer taken from mid segment of ingot

Fig. 13: Fluorescence (solid line) and absorption (dotted line) spectra for single crystals of p-terphenyl, trans-stilbene, anthracene, pyrene, and R-perylene obtained by Bridgman Method. The apparent Φ_f (fluorescence quantum yield values) are also shown [15]

In term of further research, we firmly believe that uncovering of the precise nature of the impurities (for instance, isomers of Anthracene/Stilbene) responsible for the loss of the light yield will be vital for the continuous strive to achieve improved scintillation devices. With more accurate detection and interpretation of the light yield inhibiting impurity found in Anthracene/Stilbene, we will be able to devise appropriate method to further separate such impurities from the host perhaps through combination of various refining techniques which include sublimation, column chromatography, zone melting and re-crystallization. For more details on the future work, refer to chapter 8 of the thesis.

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