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INLINE MONITORING AND PROCESS CONTROL OF REBCO TAPE PRODUCTION

A Dissertation

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the Faculty of the Department of Mechanical Engineering

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

in Materials Engineering

by

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Inline Monitoring and Process Control of REBCO Tape Production

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Abstract

High Temperature Superconducting (HTS) Coated Conductors (CCs) based on epitaxial $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (REBCO, RE = rare earth) thin films with superior mechanical properties and high current carrying capacity are being developed for various large-scale electric power and magnetic applications. The critical current density (J_c) of REBCO coated conductors in a magnetic field is higher than that of any other HTS. However, further J_c enhancement in REBCO coated conductors, particularly in magnetic fields perpendicular to the plane of the tape ($B \parallel c$) is necessary due to the highly anisotropic nature of REBCO films. The inherently high in-field angular anisotropy of J_c of REBCO CCs can be diminished by introducing Artificial Pinning Centers (APCs) with optimal size, geometry, and density. The incorporation of a high BaMO_3 (BMO; M=Zr, Hf, Sn) dopant concentration in REBCO films to achieve a higher density of nanoscale defects has been demonstrated via multiple routes of MOCVD processing as a very effective strategy to pin the vortices, especially in moderate-to-high applied magnetic fields and low temperatures. Manufacturing high quality REBCO tapes at scale with excellent homogeneous magnetic field performance pose a major challenge. Using XRD as an inline monitoring tool, it has been demonstrated that the quality of the tapes can be monitored in real time by tracking the lattice parameter of REBCO and secondary phase nanorod dimensions. In-field magnetic performance parameters measured using the Physical Property Measurement System (PPMS) and chemical compositional information obtained using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) were correlated to the properties measured in real-time using XRD, which will play an instrumental role in ensuring chemical and physical homogeneity of the tapes when manufactured at scale. A custom gas cell with FTIR instrumentation has also been demonstrated as an excellent tool for tracking the chemical homogeneity of the vapor composition in real time and potentially being utilized for real time feedback control. The ICP – MS was also improved and standardized using novel techniques such as Continuous Calibration Verification (CCV) to

monitor drift in the measurements and an Octopole Reaction System (ORS) was installed to remove potential interferences from polyatomic species generated in the plasma.

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List of Abbreviations

YBCO	YBa ₂ Cu ₃ O _{7-δ}
T_c	Critical Temperature
ΔT_c	Superconducting Transition Width
J_c	Critical Current Density
I_c	Critical Current
J_e	Engineering Critical Current Density
H_c	Critical Magnetic Field
H_{c1}	Lower Critical Magnetic Field
H_{c2}	Upper Critical Magnetic Field
λ	Penetration Depth
ξ	Coherent Length
Φ_0	Quantum Flux
F_p	Pinning Force
F_L	Lorentz Force
HTS	High Temperature Superconductors
LTS	Low Temperature Superconductors
1G	First Generation
2G	Second Generation
CCs	Coated Conductors
PIT	Powder in Tube
B_{irr}	Irreversibility Magnetic Field
Bi-2223	Bi ₂ Sr ₂ Ca ₂ Cu ₃ O ₁₀
ψ	Superconducting Order Parameter
FLL	Flux Line Lattice
BZO	BaZrO ₃
REBCO	REBa ₂ Cu ₃ O _{7-δ} (RE=Gd, Y)

APCs	Artificial Pinning Centers
IBAD	Ion Beam Assisted Deposition
ISD	Inclined Substrate Deposition
RABiTS	Rolling Assisted Biaxially Textured Substrate
MOCVD	Metal Organic Chemical Vapor Deposition
MOD	Metal Organic Deposition
PLD	Pulsed Laser Deposition
THF	Tetrahydrofuran
SCCM	Standard Cubic Centimeters per Minute
HRXRD	High Resolution X-ray Diffraction
GADDS	General Area Detector Diffraction System
ICP-MS	Inductive Coupled Plasma – Mass Spectrometry
SEM	Scanning Electron Microscope

TEM

Transmission Electron
Microscope

Chapter 1

1. Introduction

This chapter will serve as an introduction to the physics of superconductivity, flux pinning in superconductors, substrates used for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) thin film growth, YBCO fabrication processes, and applications of YBCO coated conductors. This will serve to illuminate the diverse aspects and motivations behind the ideas presented as part of this research work.

1.1 Superconductivity overview

The most important property of superconductors is their ability to carry electrical current with zero resistance. [1] Superconductivity is a property exhibited by certain materials to display zero resistance when cooled below a certain temperature. The temperature at which the superconductors lose their electric resistance is called the critical temperature (T_c), and the width of transition from the normal state ($T > T_c$) to the superconductor state ($T < T_c$) is known as the superconducting transition width (ΔT_c). The decrease in resistivity of conductors with temperature is illustrated in Figure 1-1. The zero resistance of superconductors is due to the weak coupling of a conduction electron with another in the form of pairs, which are known as Cooper pairs. There is no scattering of the individual pairs by atoms or impurities, and therefore the superconducting current consisting of these pairs can flow without any dissipation. The superconducting order parameter ψ is used to denote the ordering present in these correlated electron pair systems. Above T_c , as illustrated by Figure 1.1, we can clearly see that the material is in the normal conducting state i.e., it exhibits no order, $\psi = 0$. Below T_c , it enters the superconducting state and ordering in the electron system arises i.e., $\psi \neq 0$. These pairs are expressed by wave functions with exactly the same amplitude and phase and these over each other, resulting in a *macroscopic wave function*. This macroscopic wave function is given by the aforementioned order parameter ψ . Moreover, a variety of other

aspects of superconducting phenomena like *persistent current*, the *Meissner effect*, the *Josephson effect* etc. appears.

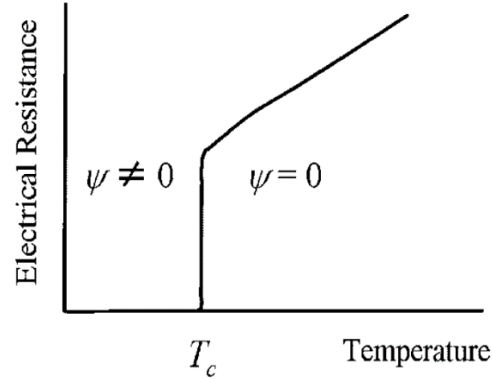


Figure 1.1 A typical temperature dependence of an electrical resistance of a superconductor. T_c is transition temperature. When $\psi \neq 0$, ($T < T_c$) the material is in the superconducting state, whereas $\psi = 0$ ($T > T_c$) corresponds to the normal conducting state.

Heat loss due to electrical resistance occurs when current is passed through a normal conductor like copper or aluminum. Such a disadvantageous energy loss in electric power cable cannot be disregarded. At high enough values of current density, a coil made out of copper wire to generate a strong magnetic field would disintegrate due to this heating, whereas no such energy loss occurs if a similar current is applied to a superconductor of the same cross sectional area as that of the copper wire, below T_c , since the superconductor has *zero electrical resistance*. Thus a strong magnetic field can be generated by a superconducting coil and power can be transmitted over long distances using a superconducting cable with no energy losses.

Figure 1.2 show the evolution of critical temperature T_c of superconductors. The superconductivity of mercury was discovered first by Kamerlingh – Onnes in 1911 [2]. Further discoveries of superconducting materials followed and T_c rose slowly. Cuprate superconductors were discovered in 1986 [3,4], and after this, the T_c increased rapidly [5] reaching 164 K at the high pressure of 30 GPa [6]. This means that the maximum T_c had already reached halfway towards room temperature (~ 300 K). These materials are called *high – T_c superconductors*. The metallic superconductor MgB_2 , with $T_c = 39$ K, was

discovered in 2001. [7]. More recently, a new material group with $T_c \approx 56$ K was discovered in 2008, this being an iron pnictide, containing iron and arsenide instead of copper and oxygen [8, 9] and this advancement has led to renewed interest in high – T_c superconductors.

Conventional Nb-Ti and Nb₃Sn superconducting wires are already being put to practical use [10], and the effectiveness of these superconductors has been confirmed by the development of magnetic levitation trains, Magnetic Resonance Imaging (MRI), Nuclear Magnetic Resonance (NMR), particle accelerators *etc.* These metallic wires are also essential for the construction of the large – scale superconducting coil of a nuclear fusion device, but they need to be cooled down to 4.2 K with the aid of expensive liquid helium.

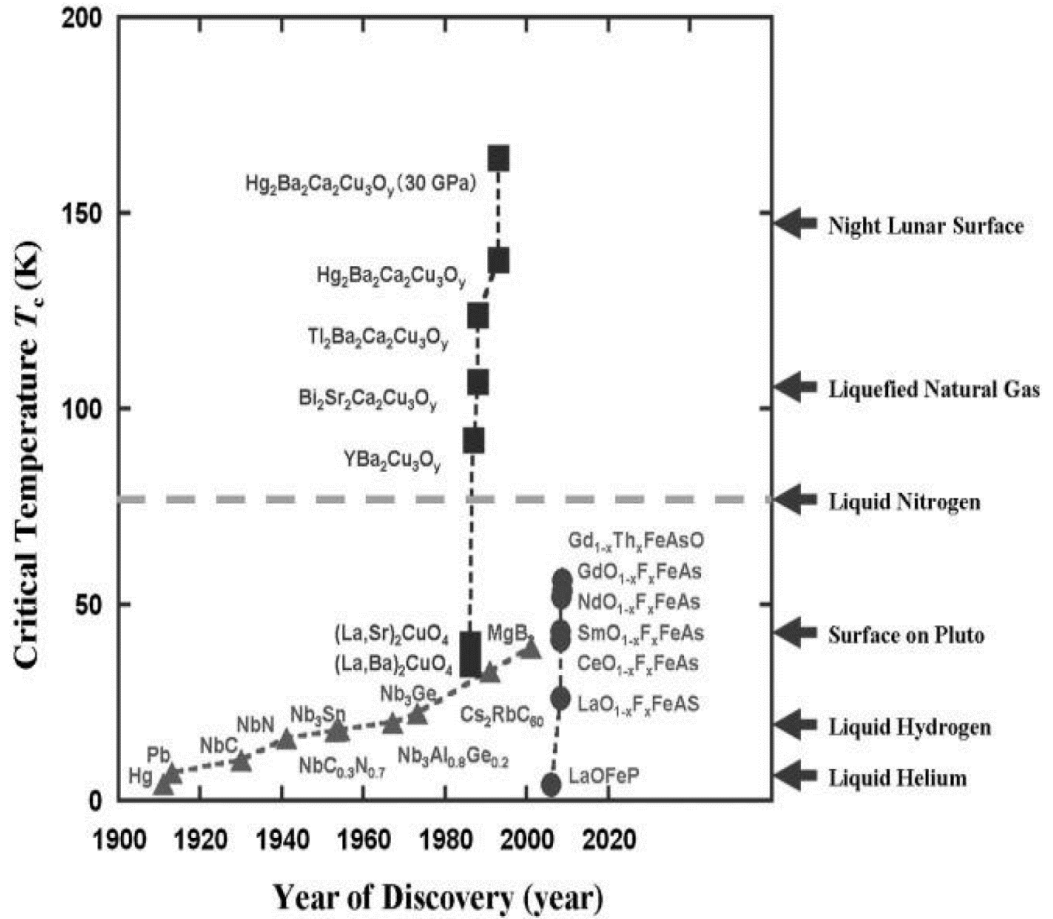


Figure 1.2 The evolution of the critical temperature T_c of superconductors. The series of high – T_c cuprate superconductors were first discovered in 1986. Iron arsenide superconductors which are other candidates for high- T_c superconductors, were discovered in 2008.

The critical temperature of the high- T_c superconductors has now exceeded 77 K, so that their electrical resistance becomes zero in liquid nitrogen. Abundant quantities of nitrogen are available in the atmosphere, so that the cost of cooling is greatly reduced, since liquid nitrogen is substantially less expensive than liquid Helium. The application of high- T_c superconductors to electric power energy and transmission is expected to revolutionize the electric grid in the 21st century.

1.2 Type I and Type II Superconductors

In the framework of the Ginzburg Landau theory, [12], two degrees of freedom of the phase and the amplitude are included in the order parameter. The characteristic lengths that show spatial correlations of the phase and the amplitude are the GL *penetration depth* $\lambda(T)$ and the GL *coherence length* $\xi(T)$. These lengths are temperature dependent quantities and vary as $(1 - T/T_c)^{-1/2}$ with temperature. The ratio $\kappa = \lambda(T)/\xi(T)$ is called the *GL parameter* and is an important factor based on which the magnetic characteristics of the superconductors are decided.

In order to study the influence of κ on the superconducting state, assume a case where the magnetic field H is applied to the superconductor as shown in Figure 1.3. When the external magnetic field H_e invades the superconductor locally, superconductivity is lost in an area of ξ radius and the magnetic field energy is decreased in an area of λ radius where the magnetization is zero; therefore the free energy of $G_{core} = (1/2)\mu_0 H_c^2 \pi \xi^2$ per unit length is increased whereas $G_{mag} = (1/2) \mu_0 H_c^2 \pi \lambda^2$ per unit length is decreased. The total free energy is then computed as

$$G = G_{core} + G_{mag} = (1/2)\mu_0 H_c^2 \pi \xi^2 - (1/2) \mu_0 H_c^2 \pi \lambda^2 . \quad (1.2)$$

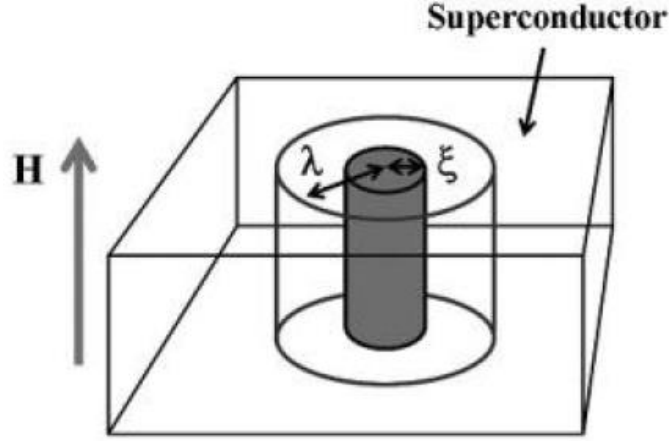


Figure 1.3 Virtually invaded external magnetic field H in the superconductor. The order parameter is lost locally in an area of radius ξ and the condensation energy increases there, whereas the magnetic field penetrates in the area of radius λ and magnetic energy is decreased.

From equation 1.2, it can be seen that the destruction of part of the superconducting area is favored when $G < 0$, but the magnetic field is excluded when $G > 0$. Defining the *lower critical field*, $H_{c1} = (\xi/\lambda)H_c$ by assuming $G = 0$ with $H_e = H_{c1}$, we are likely to have $G < 0$ with $H > H_{c1}$ at $\kappa > 1$. According to the more accurate calculations based on GL theory, the boundary between $G < 0$ and $G > 0$ is given by $\kappa = 1/\sqrt{2}$ and $H_{c1} = (H_c / \sqrt{2\kappa}) \ln \kappa$ is derived. Thus, we can obtain the following criteria:

- | | | | |
|----|-----------------------|--------------|-----------------------------------|
| a) | $\kappa < 1/\sqrt{2}$ | $H < H_c$ | Meissner state. |
| | | $H > H_c$ | Normal conducting state. |
| b) | $\kappa > 1/\sqrt{2}$ | $H < H_{c1}$ | Meissner state. |
| | | $H > H_{c1}$ | Magnetic field invades partially. |

A superconductor in condition (a) is called *type I superconductor*, and one in condition (b) is called *type II superconductor*. Figure 1.4 shows the magnetic phase diagrams of type I and type II superconductors. The commercially-important type that will be treated in the rest of treatise will be of type II.

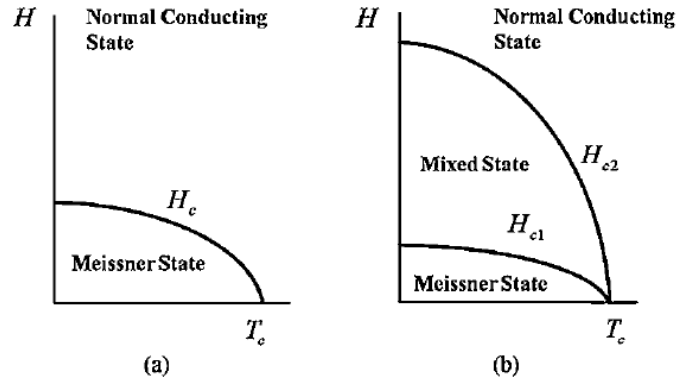


Figure 1.4 Simplified magnetic phase diagrams for (a) type I superconductor and (b) a type II superconductor. The H_c , H_{c1} and H_{c2} lines separate the Meissner state, the mixed state and the normal conducting state.

1.3 Mixed State

When a magnetic field $H > H_{c1}$ is applied to a type II superconductor, the superconductor enters the mixed state where the magnetic field starts to penetrate the superconductor in the form of quantized vortices. This phenomenon is explained in the following section.

In a type II superconductor, the magnetic field invades in the form of many vortices when $H > H_{c1}$, and this is called the *mixed state*. The cross-sectional structure of a vortex is shown in Figure 1.5

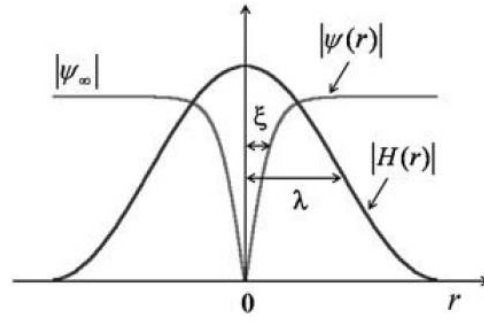


Figure 1.5 Schematic diagrams of the vortex structure in a type II superconductor. The vortex has a normal conducting core with radius ξ and is surrounded by a magnetic field with a radius of λ . The confined magnetic flux is quantized, and its value is $\phi_0 = 2.07 \times 10^{-15} \text{ Wb}$.

Since $\lambda > \xi$ in a type II superconductor, the individual vortex line has the normal conducting core with radius ξ and is surrounded by a magnetic field with radius λ . This structure is also called the *flux line*. The shielding current with zero resistance flows in the area of radius λ of the vortex and the magnetic flux is confined within this area. The confined magnetic flux is quantized and is called as the *fluxon*, its value being $\phi_0 = 2.07 \times 10^{-15} \text{ Wb}$. This is referred to as the *quantization of the magnetic flux*. It should be noted that the definition of the term flux line applied to the conventional type II superconductors. However, in the extreme type II superconductors such as high- T_c cuprate superconductors, the definition of the flux line becomes difficult as λ much larger compared to ξ , so that the concept of the vortex line becomes important.

The Meissner state of $M = -H$ is observed in the M - H curve where $0 < H < H_{c1}$, as shown in Figure 1.6(a).

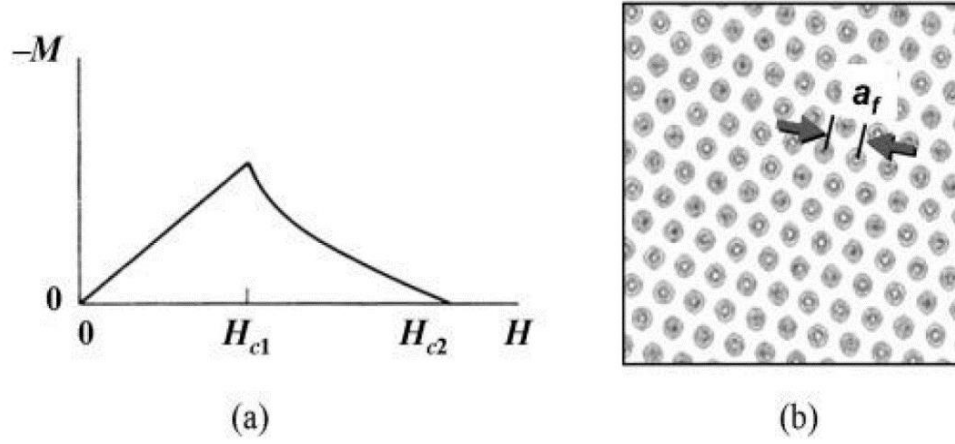


Figure 1.6 (a) Magnetic field dependence of magnetization in a type II superconductor (b) the typical triangular lattice of vortices in a pure superconductor.

In the mixed state where $H > H_{c1}$, the superconductivity is maintained up to $H = H_{c2}$ where all the superconductor area is filled with the vortices. H_{c2} is called the *upper critical field*. The values of $\mu_0 H_{c2}$ ($=B_{c2}$) of metallic superconductors are around 10 – 30 T, and those of high temperature superconductors exceed 100 T. Large values of H_{c2} are one of the primary reasons as to why most of the commercially important superconductors are of type II. The upper critical field is expressed by

$$\mu_0 H_{c2} = B_{c2} = \phi_0 / 2\pi\xi^2. \quad (1.3)$$

The vortices form triangular lattices in a pure superconductor with no pinning centers as shown in Figure 1.6(b). The triangular lattice is called the *Abrikosov lattice*, *vortex lattice* or *flux line lattice*. [13]. The lattice interval a_f of the triangular vortex lattice is given by

$$a_f = (2\phi_0 / \sqrt{3}B)^{1/2}. \quad (1.4)$$

What happens when current $\mathbf{J}$ is applied to the superconductor in the mixed state? At this time the current exerts a *Lorentz force* of

$$\mathbf{F}_L = \mathbf{J} \times \mathbf{e}_z \phi_0 \quad (1.5)$$

on the vortices. Here, $\mathbf{e}_z$ is the unit vector in the Z direction. Moving the vortices at a speed of $\mathbf{v}_L$ by this force, the electric field

$$\mathbf{E} = \mathbf{B} \times \mathbf{v}_L \quad (1.6)$$

is generated. The motion of vortices is called *vortex flow* or *flux flow*. [13]. $\mathbf{v}_L$ does not increase infinitely because of the frictional force due to the surrounding environment when the vortices move, and $\mathbf{F}_L$ balances with the viscous force $-\eta\mathbf{v}_L$, where η is the coefficient of viscosity. In the vortex flow state, energy dissipation is generated even while the superconductor is in the superconducting state and that poses a major challenge from the viewpoint of commercial applications. Therefore, *vortex pinning* (or *flux pinning*), which is described in the forthcoming sections, has become technologically important.

1.4 Cuprate Superconductors

$\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ superconductor, discovered in 1986, is a copper oxide superconductor [3,4]. This material became the forerunner of the series of high- T_c superconductor discoveries, which followed. The basis of high- T_c superconductors is the CuO_2 layer. The high- T_c superconductors are also called the *Cuprate Superconductors*, and their properties are summarized in Table 1.1 [3,15].

Table 1.1 Crystal System and lattice parameters of typical high- T_c superconductors.

Superconductor	Crystal System	a (nm)	b (nm)	c (nm)
$\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$	Tetragonal	0.3790	–	1.323
$\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$	Tetragonal	0.3945	–	1.217
$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$	Orthorhombic	0.3823	0.3887	1.168
$\text{Bi}_{2.2}\text{Sr}_2\text{Ca}_{0.8}\text{Cu}_2\text{O}_8$	Orthorhombic	0.5414	0.5418	3.089
$(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	Orthorhombic	0.5404	0.5415	3.708
$\text{HgBa}_2\text{CaCu}_2\text{O}_{6+x}$	Tetragonal	0.3858	–	1.266

Figure 1.7 shows the crystal structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ cuprate superconductors. $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO or Y123) is the superconductor whose T_c was found to be above the temperature of liquid nitrogen (77 K) for the first time and reached 93 K [5]. In this material, layers of Y atoms are sandwiched between the two adjoining pyramid – type CuO_2 layers. Moreover, there is a triple periodic structure in which Y and Ba atoms are in line as Ba – Y –

Ba, and there are one – dimensional chains of Cu – O – Cu in the direction of the b – axis of the crystal.

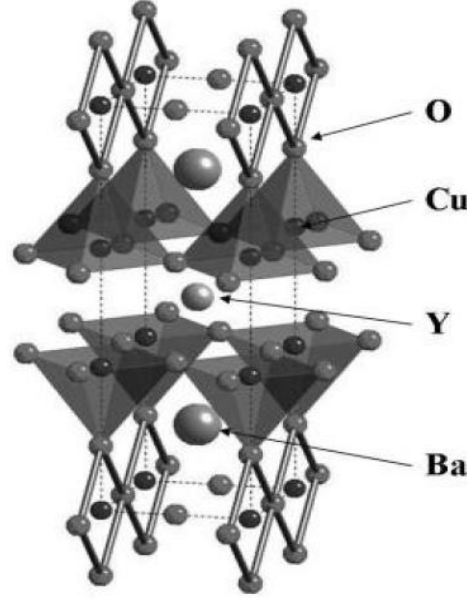


Figure 1.7 Crystal structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductor showing two adjoining pyramid – type CuO_2 planes and CuO chains in the unit cell.

The oxygen deficiency, expressed by x in the chemical formulae of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, plays an important role in the hole implantation into CuO_2 layers. The amount of the oxygen deficiency is controlled by the incorporation and removal of the oxygen ion in the CuO chains. T_c reaches a maximum of 93 K at $x \approx 0$ (orthorhombic system, Ortho I) and becomes 60 K at $x \approx 0.5$ (orthorhombic system, Ortho II), then superconductivity disappears at $x \approx 0.7$ (tetragonal system, Tetra). The lattice constants of Ortho I are $a = 0.382$ nm, $b = 0.388$ nm, and $c = 1.168$ nm, and since a local distortion is caused by the difference between the lattice constants a and b , twins are introduced to ease this distortion.

1.5 Anisotropy and Vortex lattice melting

The CuO_2 layer structure is reflected in the cuprate superconductors, and two – dimensional characteristics appear to a remarkable extent in the various physical properties. The ratio of out-of-plane resistivity ρ_c to the in-plane resistivity ρ_{ab} in the CuO_2 layer

becomes $\rho_c/\rho_{ab} \gg 1$. This means that the carriers cannot move easily in the direction of the c – axis and their effective mass m_c is relatively larger than the in – plane effective mass m_{ab} . Since the cuprate superconductors are type II superconductors, the effective mass ratio relates to the anisotropic parameter γ_a , the coherence length ξ , and the upper critical field H_{c2} , and the penetration depth λ as given by the following expressions as

$$(m_c/m_{ab})^{1/2} = \gamma_a = \xi_{ab}/\xi_c = H_{c2//}/H_{c2\perp} = \lambda_c/\lambda_{ab}, \quad (1.6)$$

where // denotes the case where magnetic field is applied parallel to the layer and $\perp$ corresponds to the perpendicular case. Using the angle θ between the direction parallel to the CuO_2 layer and the direction of the magnetic field, $H_{c2}(\theta)$ is given by

$$H_{c2}(\theta) = H_{c2//} (\cos^2 \theta + \gamma_a^2 \sin^2 \theta)^{1/2}. \quad (1.7)$$

This anisotropic model is called the *effective mass model*. [19]. Superconducting parameters of the high- T_c cuprate superconductors are summarized in Table 1.2.

Table 1.2 Superconducting parameters of the cuprate superconductors.

Superconductor	T_c (K)	λ_{ab} (nm)	λ_c (nm)	ξ_{ab} (nm)	ξ_c (nm)	$\mu_0 H_{c2\perp}$ (T)	$\mu_0 H_{c2//}$ (T)
$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$	38	100	2–5	2–3	0.3	60	—
$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$	93	150	0.8	1.6	0.3	110	240
$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$	94	200–300	15–150	2	0.1	>60	>250
$\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	107	150	>1	2.9	0.1	40	>250
$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	125	200	>20	3	0.5	28	200
$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$	135	130–200	0.7	1.5	0.19	108	—

As for YBCO and BSCCO, $\gamma_a = 5$ and $\gamma_a = 24$ are reported, respectively. In YBCO, ξ_c is shorter than the c – axis lattice constant, but ξ_{ab} is longer than the a/b/ axes lattice constant. ξ_c is extremely short in BSCCO, for example, so that the wave functions of Cooper pairs is confined in the CuO_2 layer and two – dimensional properties become remarkable. In this case, the *Lawrence – Doniach model* [20] is used to explain the anisotropic properties.

By applying the magnetic field to the high- T_c cuprate superconductor, some peculiar features are observed. For instance, (i) because the coherence length is very short, the cores of the quantized vortices are small so that the pinning strength is weak; (ii) when the vortices vertically penetrate the CuO_2 layers, the vortices bend easily because the superconducting coupling between the CuO_2 layers is weak [21]; (iii) the Abrikosov lattice easily melts in the neighborhood of T_c by the effect of thermal energy [22]. As a result, the influence of the thermal fluctuations become remarkable in cuprate superconductors, and the phase transition between the normal conducting state and the superconducting state becomes indistinct.

In the neighborhood of H_{c_2} , though the amplitude of the superconducting order parameter is developing, the phase is changing with time, and a liquid state of the vortex lattice, which has no long-range order, is formed (*vortex liquid state*). However, a solid state of the vortex lattice in which the phase freezes exists (*vortex solid state*) in the magnetic field regime considerably below H_{c_2} . Therefore, the melting transition of the vortex lattice from the vortex solid to the vortex liquid occurs in the intermediate area. This is a first – order transition. Schematic views of the *melting lines* of BSCCO and YBCO are shown in Figure 1.8. In the case of BSCCO, the area of the vortex liquid state is very wide because of the strong two-dimensional features; in contrast, the area of the vortex liquid state is comparatively narrow in YBCO.

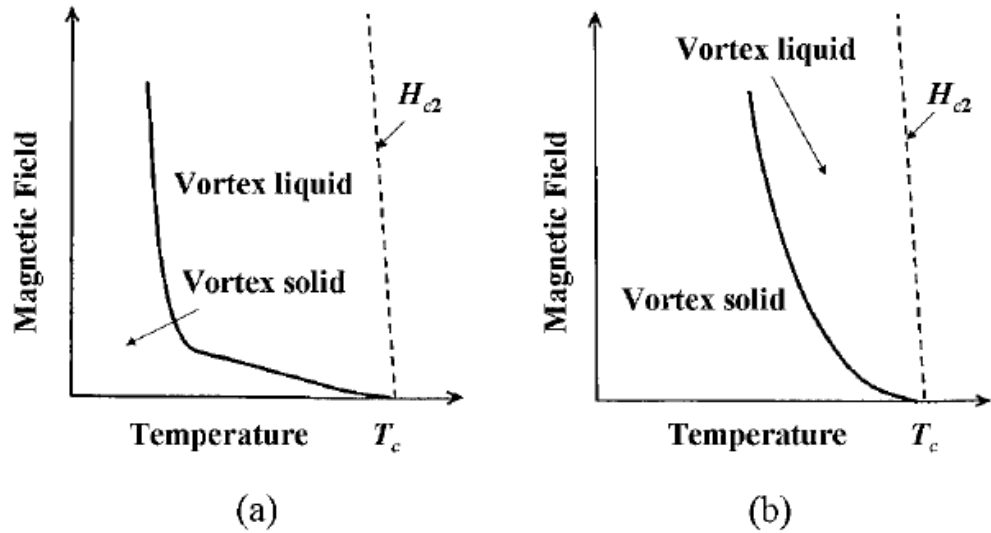


Figure 1.8 Comparison of the melting lines and H_{c2} lines for (a) BSCCO (b) YBCO. The vortex liquid area of BSCCO is wider than that of YBCO.

1.6 Critical currents and Vortex Pinning

In this section, the relationships between critical currents and vortex pinning (or flux pinning) are briefly explained.

1.6.1 Current – Voltage Characteristic

It is of both scientific and engineering importance to understand the Current – Voltage (or $I - V$) characteristics of superconductors in order to appreciate and apply these materials towards commercial technologies. The maximum current obtained is called the *critical current* I_c . The critical current per unit cross sectional area of a superconductor is called the *critical current density* J_c . The typical change from zero – resistance state to the finite resistance state by applying the current to the superconductors is shown in Figure 1.9. The current when the voltage is generated corresponds to I_c . The electrical resistivity standard that is conventionally used to determine the onset of the normal conducting state is $10^{-14} \Omega\text{m}$ and the electric field standard is $1 \mu\text{V cm}^{-1}$. The vicinity of I_c is the regime where *vortex creep* (or the *flux creep*) becomes significant. The regimen of vortex flow (or flux flow) appears on

the high current side; and the condition where Ohm's law is obeyed appears by increasing the current. The low voltage area below the vortex flow region is represented by the power law as

$$E(I) \propto (I/I_c)^n, \quad (1.8)$$

where the power n is called the n value, which is an index value that shows the characteristics of superconducting material.

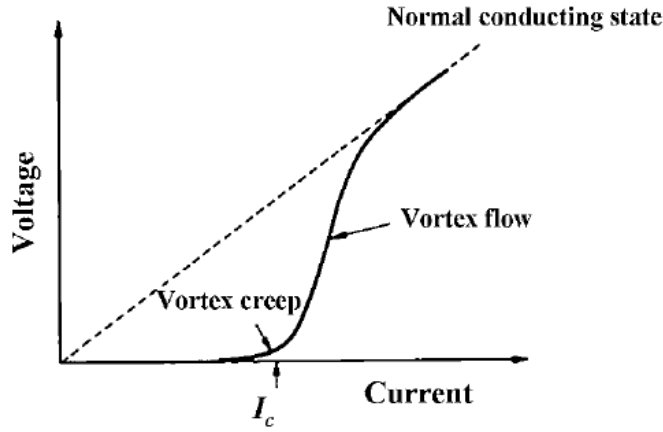


Figure 1.9 Current – Voltage characteristics of superconductors. The critical current I_c is usually determined by the electrical resistivity standard such as $10^{-14} \Omega\text{m}$ or the electrical field standard $1 \mu\text{V cm}^{-1}$.

Figure 1.10 is a schematic illustration of a case where operational criteria require regimes of lower electric field than can be measured by direct transport. Over a range of several decades in the electric field, measurements typically yield voltage – current relationships that obey a power law, $E \propto J^n$, with an exponent (the ‘index’ or n -value) indicative of the current – induced moving vortices. The features of this exponent are of fundamental interest because they reflect the nature of non-uniform vortex motion. The n -value is also of significant practical importance, because the level of the ‘index losses’, $w = E.J \propto J^{n+1}$, is the heat per unit volume that will be generated within the superconductor at the operating current density J . For most applications, a material with higher n values is generally

more desirable because small reductions in operating J values lead to drastically smaller E , thereby reducing the intrinsic index losses.

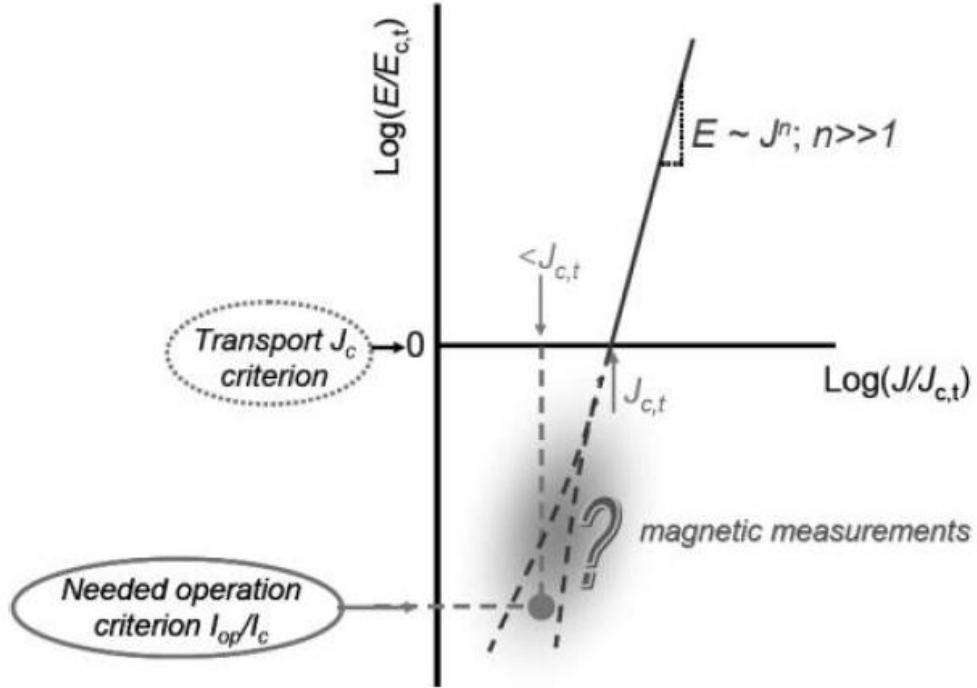


Figure 1.10 A schematic representation of the highly nonlinear electric field vs current density relation for a superconductor. The E – field criterion $E_{c,t}$ that defines the critical current J_c is too dissipative for some applications.

Since the $E - J$ characteristics effectively encapsulates the conductive and vortex state properties of the material and therefore strongly affect the electromagnetic behavior of high-temperature superconducting devices, it is extremely useful to investigate the $E - J$ characteristics over a wide span of electric and magnetic fields over a wide temperature range. From Figure 1.11, we can see that at the operating condition, the value of n may have evolved to either higher or lower values, and may not be known *a priori*. For measurements on small samples in the laboratory, the instrumental voltage resolution and voltage tap spacing as show schematically in Figure 1.11(a) generally limits the lowest transport electric field level. Figure 1.11(a) is a schematic representation of a transport current measurement on a laboratory scale sample. The range of accessible currents and voltages in determining $E(J)$ is often limited by the sample size and instrumental resolution. Typical electric fields are $\sim 10^{-6}$

V cm^{-1} . Fig 1.11(b) is a schematic of a contactless measurement of $E(J)$ by measuring the supercurrent induced magnetic moment, where E is determined by the change of flux under a constant magnetic field sweep rate dH/dt . Here electric field levels are $10^{-7} - 10^{-9} \text{ V/cm}$. Fig 1.11(c) is a schematic diagram of contactless measurement where the electric field is induced by a time decay of the supercurrents.

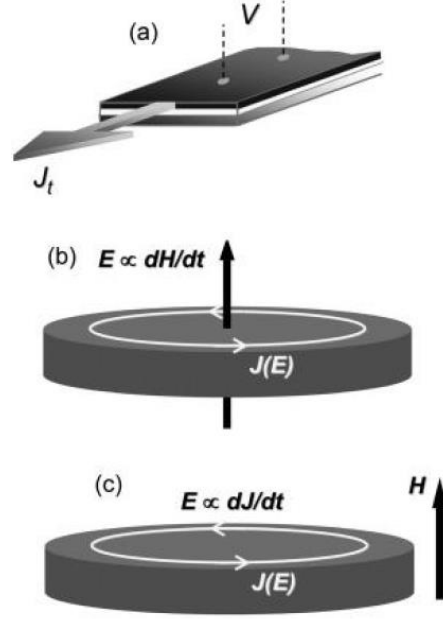


Figure 1.11 (a) Schematic representation of a (a) transport current measurement (b) A contactless measurement of $E(J)$ by measuring the supercurrent induced by magnetic moment (c) Contactless measurement where the electric field is induced time decay of the supercurrents.

1.6.2 Depairing Current Density

The most important feature of a superconductor is its ability to carry current without electrical resistance. The formation of Cooper pairs according to BCS theory [11] and the energy gap 2Δ are related to this phenomenon. An individual electron in the normal conducting state is scattered by phonons and by impurities, and its direction of movement is forced to change; hence, electrical resistance is generated.

When the current is flowing, an individual Cooper pair is not permitted to change its direction of movement because of the strong interaction between the pairs. This is feasible

only after a Cooper pair breaks up, but for this purpose, kinetic energy equivalent to the energy gap must be induced in the Cooper pairs by the flowing currents. This limiting value of current is called the *depairing current*.

The maximum theoretical critical current density in the superconductor can be estimated by equating the kinetic energy of the Cooper pair to the energy gap 2Δ . At this point, the pair is destroyed and the maximum value is achieved which can be expressed as

$$(1/2)m^*v_F^2 = 2\Delta, \quad (1.9)$$

where v_F is the Fermi velocity and $m^* = 2m$. A rough estimation is obtained by substituting v_F for $J = e^*n_s v_F$. A more accurate value can be derived from GL theory as

$$J_d = \phi_0 / (3\sqrt{3}\pi\mu_0\lambda^2\xi). \quad (1.10)$$

J_d is called the *depairing current density*. The calculated J_d values of some superconducting materials is summarized in Table 1.3 [23]. Although the current density in a copper wire under conditions without a significant energy loss is usually around $10^2 - 10^3 \text{ Acm}^{-2}$, superconductors can carry a maximum current density that is around $10^5 - 10^6$ times larger than that in copper without energy loss. However, the J_c of practical superconducting wires has not yet reached this theoretical limit. This is because the voltage generation in the current – voltage characteristic is decided by the strength of vortex pinning.

Table 1.3 Depairing current density J_d and the observed J_c for typical superconductors [circa 2008].

Superconductor	T_c (K)	J_d (MA cm ⁻²)	J_c (MA cm ⁻²)	J_c/J_d
NbTi	9	36	~2 (4.2 K, 0 T)	6%
Nb ₃ Sn	18	770	~2 (4.2 K, 0 T)	0.3%
MgB ₂	39	77	~1 (4.2 K, 0 T)	1.3%
YBa ₂ Cu ₃ O _{7-x}	93	~300	~20 (4.2 K, 0 T)	7%
Bi ₂ Sr ₂ Ca ₂ Cu ₃ O ₁₀	110	~300	~0.3 (4.2 K, 0 T)	0.1%

(MA cm⁻² = 10⁶ A cm⁻²).

1.6.3. Vortex Pinning

When a perfect crystal with no defects present in it behaves as a type II superconductor and enters the mixed state, upon application of a current, vortex flow is induced by the Lorentz force. However, in real crystalline materials, some defect will always be present and these defects exert pinning forces which stem the vortex flow against the Lorentz forces on the vortices. This is *vortex pinning* and these defects are called *pinning centers*. The pinning centers are classified as follows from their dimensions.

0D - Point defect, oxygen vacancy

1D – Dislocation, columnar defects, nanorods etc.

2D - Grain boundary, planar precipitate, stacking fault, interface etc.

3D – Voids, Precipitates.

The interaction between the defect and the vortex is generated through various mechanisms depending upon the size and dimension of the defect. For instance, suppose there is a small normal conductive precipitate and a single vortex that is outside the precipitate in the superconductor, as shown in Figure 1.12. The superconductivity in the cylindrical normal core of the vortex is lost and the order parameter ψ is zero at the core. Therefore, the total energy increases by the condensation energy of the core volume when the vortex stays in the superconducting region. However, if the vortex is located in the precipitate, the energy

penalty, which is proportional to the condensation energy of the intersection volume between the normal core and the precipitate, is canceled. This energy difference gives the following pinning energy U_p as

$$U_p = (1/2)\mu_0 H_c^2 \pi \xi^2 d, \quad (1.10)$$

where d is the length of the vortex that intersects with the precipitate. The *elementary pinning force* f_p exerted by the precipitate is given by the maximum value of the energy change by moving the vortex across the precipitate [4, 32, 33] and is approximated by

$$F_p = U_p/\xi = (1/2)\mu_0 H_c^2 \pi \xi d. \quad (1.11)$$

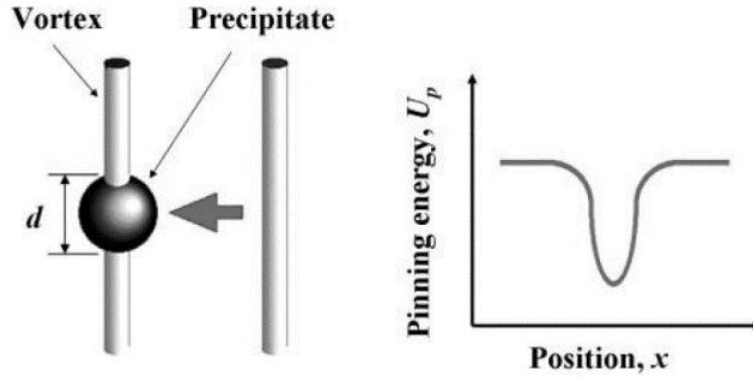


Figure 1.12 Flux pinning of vortex due to the normal conducting precipitate. The pinning energy U_p is estimated as $(1/2)\mu_0 H_c^2 \pi \xi^2 d$.

The grain boundary is also another important pinning center. The electron is scattered in the vicinity of the grain boundary, and its mean free path l shortens. Because the coherence length ξ obeys the relationship $\xi \propto \sqrt{l}$, ξ becomes small as l decreases. This means that the size of the normal core is reduced and the area in which the superconductivity is lost becomes small, as the vortex approaches the grain boundary. When the vortex is located in the grain boundary, an energy gain is obtained, and this energy difference functions as the pinning energy [24, 25].

Though these are the core interactions that arise from the normal core of the vortex, there is also the magnetic interaction that stems from the change in the distribution of the

superconducting current that flows in the circumference of the vortex. If there is a planar precipitate whose thickness is thinner than ξ in the superconductor, the distribution of the superconducting current that flows around the vortex changes as the vortex approaches the precipitate, and a *Josephson vortex* is formed. The core disappears in the Josephson vortex and only the shielding current flows, expanding along the precipitate to achieve the quantization of magnetic flux. Such a thin planar precipitate also gives the pinning interaction that nearly equals the core interaction, and the strong elementary pinning force is thought to be yielded. [26].

1.6.4. Global Pinning Force

The Lorentz force that is exerted on an individual vortex balances with the pinning force of the pinning center, and the vortex is pinned there until the Lorentz force exceeds f_p . The maximum pinning force per unit volume achieved with a large number of pinning centers is called the *global pinning force* $\mathbf{F}_p$, and is given by

$$\mathbf{F}_p = \mathbf{J}_c \times \mathbf{B}. \quad (1.12)$$

$\mathbf{F}_p$ is also expressed as a function of the elementary pinning force f_p and the pin density N_p . The problem of obtaining $\mathbf{F}_p$ at a certain temperature and in a certain magnetic field is called a *summation problem* under the condition of given f_p and N_p [32, 33, 45]. This is a many-body problem where the elastic energy between vortices competes with the pinning energy. Furthermore, the thermal energy is added to this in the case of high- T_c superconductors. Let us first consider the case in which the vortex lattice is not deformed by the pinning, since f_p is extremely small and the rigidity of the vortex lattice is relatively high. If the pinning centers exist at random, the vortex lattice experiences small random forces. As a result, the resultant force is

$$F_p = |\mathbf{F}_p| = \Sigma f_p = 0. \quad (1.13)$$

In this case, J_c is zero. This is called the *weak pinning limit*. Figure 1.13 shows such a condition. In contrast, in the *strong pinning limit* in which f_p is extremely large and the vortex lattice is deformed freely, each vortex can be pinned by the strong pinning centers as shown in Figure 1.13. We can obtain the relation of

$$F_p = |\mathbf{F}_p| = \Sigma f_p = N_p f_p. \quad (1.14)$$

This is the *direct summation*, where the maximum J_c which can be achieved by the pinning is given. [33,46]. But, F_p of actual superconductors is located in between these two limits. In addition, if f_p is so small that the vortex lattice behaves collectively, we can estimate the value of F_p on the basis of the *collective pinning model*. [45]. This model is often applied to the interpretation of the vortex pinning in high- T_c superconductors.

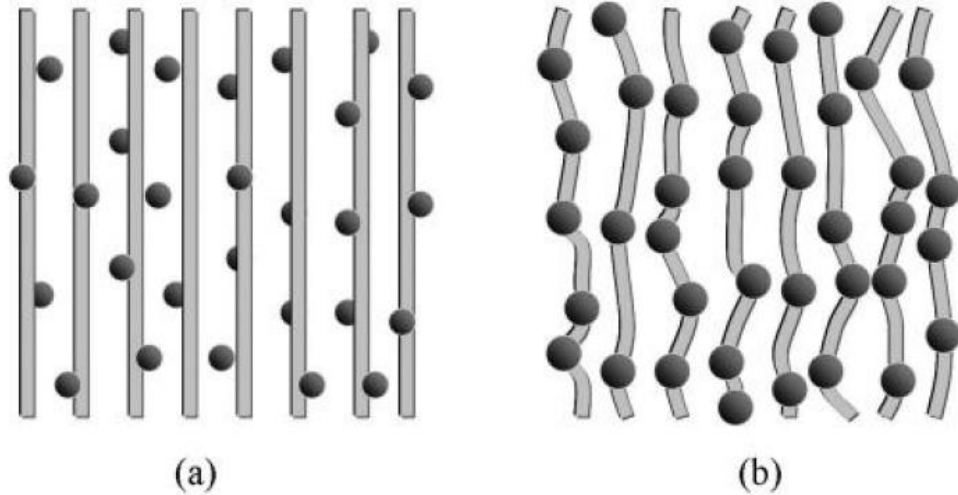


Figure 1.13 Comparison of configuration of vortices trapped by the pinning centers: (a) Weak pinning centers, and (b) strong pinning centers.

1.7 Grain Boundary Problem

Although the cuprate superconductors are advantageous since the T_c values are very high compared with those of conventional superconductors, features such as the crystalline anisotropy and the short coherence length ξ must be considered. These pose some major

challenges when it comes to practical applications. Figure 1.14 shows a grain boundary in a superconductor on an atomic scale. For instance, the spatial distribution of the order parameter ψ in the interface of grain 1 and grain 2 should be considered. Although the order parameters in each of the grains decrease at the grain boundary, a ψ of sufficient size remains by overlapping both in the boundary if ξ is 5 nm, for instance. However, ψ in the grain boundary is almost lost if ξ is short (e.g., 1 nm) and the superconducting characteristic deteriorates. Therefore, the superconducting current flowing across the grain boundary becomes extremely small in the cuprate superconductors. [47].

Figure 1.15 shows the relationship between the J_c at the grain boundary and the misorientation angle θ of the adjacent crystal grain in the YBCO bicrystal film [48]. If the misorientation angle θ is five degrees or less, the J_c is not so badly affected, but if the angle becomes larger, the J_c decreases rapidly. This is because the number density of dislocations, which are insulators, increases at the grain boundary as θ increases. In polycrystalline YBCO, where the crystal grains in various azimuths exist together, the superconducting current through the many grain boundaries becomes very small. Such a grain boundary problem has for some time seriously obstructed the development of high- T_c superconductors, but after nearly 20 years of material science and engineering R&D, special flexible buffer substrates have been developed which have enabled the production of these high T_c materials in long lengths.

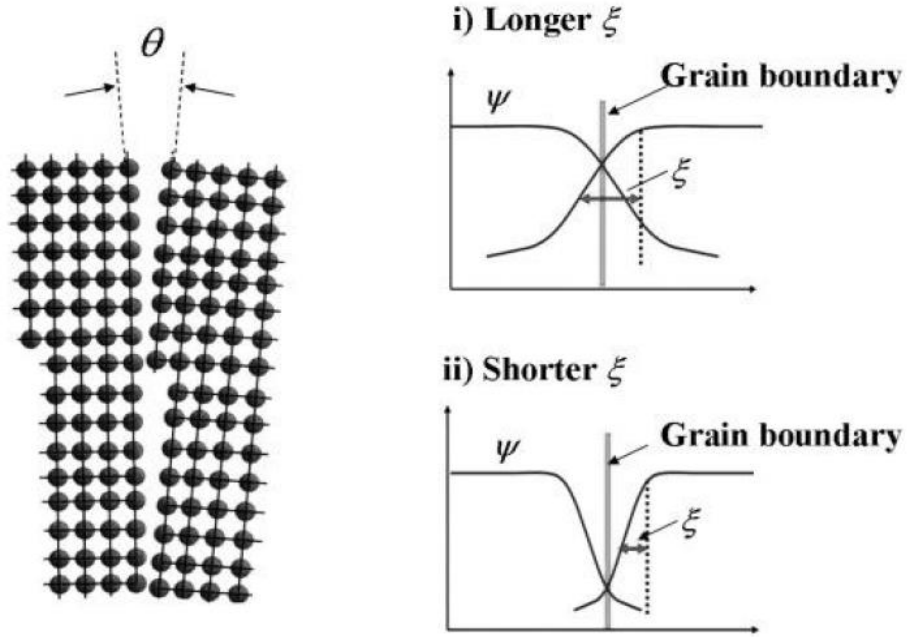


Figure 1.14 Schematic of a grain boundary with misorientation angle θ in the superconductors. The order parameter ψ is reduced at the grain boundary if the ξ is short.

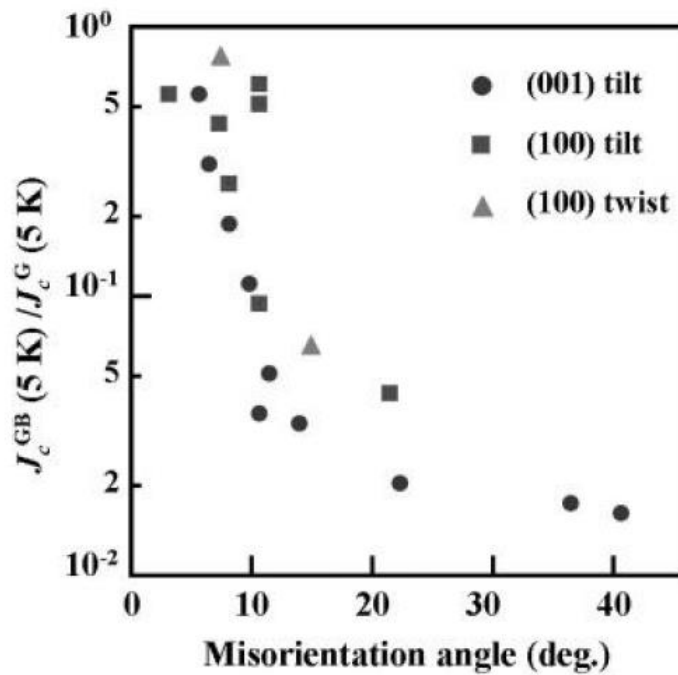


Figure 1.15 Experimental results of J_c deterioration as a function of misorientation angle in the YBCO bicrystal film. J_c decreases exponentially as the misorientation angle increases.

1.8 Buffer Substrate Engineering

Producing single crystal substrates in long lengths is an impractical proposition. Therefore, there is a need for polycrystalline substrates that can enable the epitaxial growth of HTS thin films. The choice of the right substrate is one of the most important issue in the fabrication of REBCO coated conductors (CC). To obtain REBCO thin films of high quality, the substrates must possess some of the important properties listed below:

- 1) **Similar Thermal expansion coefficient:** Mismatch between the coefficients of thermal expansions of the substrate and the crystal may result in the loss of adhesion or film cracking during thermal cycling. Considering the fact that REBCO is a brittle ceramic, this property plays a major role in maintaining the mechanical integrity of the epitaxial structure. It has been shown by Utke et al [49] that the thermal expansion coefficients of a substrate with a buffer layer and a superconducting film needs to be matched within 10 %.
- 2) **Chemical compatibility:** Chemical inertness of the buffer substrate chemistry with respect to the REBCO crystal is highly desirable. Oxide substrates such as strontium titanate (SrTiO_3), magnesium oxide (MgO), yttria stabilized zirconia (YSZ), and lanthanum aluminate (LaAlO_3) have all been demonstrated successfully to show excellent results with the high temperature growth of rare earth barium copper oxides coated conductors. (REBCO CC) at approximately 750 – 850 °C.
- 3) **Surface Quality:** Surface roughness has a significant effect on nucleation, morphology and structure of the resulting film. Surface roughness of the substrate has been demonstrated to affect the physical properties of the epitaxial crystal grown on it in terms of both orientation and microstructure. B.H. Moeckly et al [50] found that the best structural and superconducting properties of YBCO resulted from growth on MgO substrates, which are annealed in comparison with substrates that are chemically and mechanically polished. Thermal annealing yields a high density of

atomic steps, improved epitaxial c – axis growth of YBCO films and overall improvement of superconducting properties.

- 4) **Lattice matching with the REBCO film:** Lattice matching of the substrate and the REBCO film is a prerequisite for the epitaxial growth of REBCO CCs.
- 5) **Suitable mechanical properties:** Flexibility, robustness and resistance to delamination are important from a mechanical standpoint of coated conductors.
- 6) **Easy scalability to long lengths:** For any meaningful commercial applications, we need materials that can be produced in long lengths with relatively homogeneous properties that do not vary substantially from run to run.

Normally, metallic substrates with minimal or nonmagnetic hysteresis losses in the presence of a magnetic field are preferred for the application of coated conductors. Therefore, iron and its magnetic alloys are usually ruled out as suitable due to their magnetic behavior and tendency to oxidize at higher temperatures during REBCO deposition. Among the metallic candidate substrates, Ni and its alloys exhibit excellent stability and resistance to oxidation at elevated temperatures [52].

Generally, REBCO CCs are grown on metallic substrates over which other buffer layers can be grown epitaxially prior to REBCO layer. The two predominantly used methods are Ion Beam Assisted Deposition (IBAD) and Rolling Assisted Biaxially Textured Substrates (RABiTS), which are briefly discussed below.

1.8.1 IBAD and RABiTS Templates

Currently, HTS CCs are based on YBCO or similar cuprate oxides with the chemical formula of $\text{REBa}_2\text{Cu}_3\text{O}_{7-x}$ (RE = Gd, Y, Sm, Nd, Dy, Eu, Ho). Growth of high J_c YBCO thin films requires epitaxy and uniaxial texture is certainly not sufficient. Microstructures of the materials with various types of grain alignments are schematically shown in Figure 1.16.

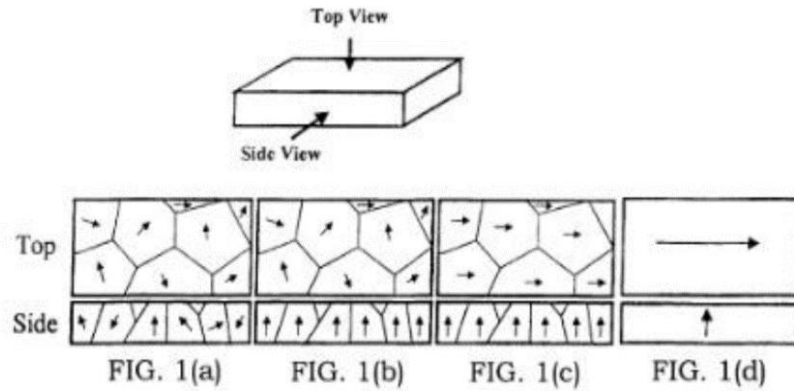


Figure 1.16 Schematic illustration of materials with (a) randomly oriented crystal grains (b) Uniaxially textured, (c) Biaxially textured, (d) Single crystal structure.

As can be seen from Figure 1.17(a), IBAD architecture starts from an untextured metallic tape (e.g., Hastelloy) and uses IBAD technique to grow the biaxially-textured buffer layer [56]. In IBAD architecture, because the substrate need not be textured, various metals could potentially be used as a substrate but Hastelloy (a Ni – based superalloy) is the preferred choice due to its high temperature stability and oxidation resistance. [57]. The RABiTS architecture starts with a biaxially textured metallic substrate of Ni or Ni – alloy made by a thermo-mechanical process [58, 59]. The biaxially – textured Ni substrates in the RABiTS process are formed by consecutive rolling of a Ni polycrystalline bar with high purity (99.99 %). The total deformation is greater than 90 percent, followed by annealing and then the epitaxial deposition of the buffer layers.

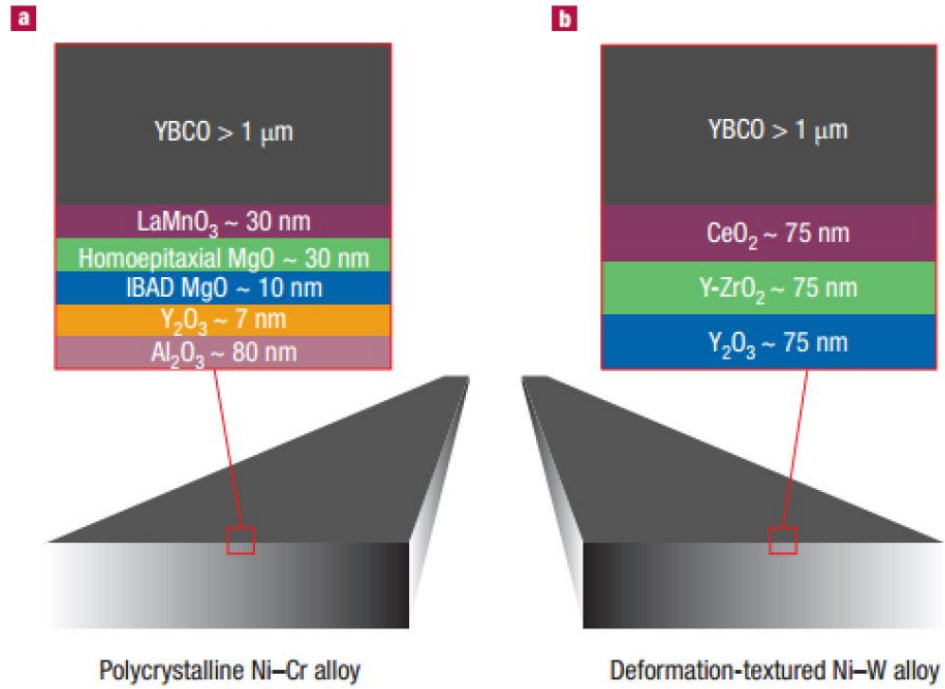


Figure 1.17 (a) Ion – Beam Assisted Deposition (IBAD) and (b) Rolling Assisted Biaxially Textured Substrate (RABiTS).

The IBAD process is shown in Figure 1.18[60-62]. The ions are either inert, such as Ar^+ , or a reactive gas such as N^+ . The deposited atoms are produced by ion – beam sputtering of a target (in this case YSZ, as shown in Figure 1.23). The assist ions (in this case, Ar^+), as shown in Figure 1.23 impinge on the growing film at an optimized incident angle to maximize the degree of in – plane alignment of the thin film. Wang et al. [53] found that MgO is a better template than YSZ for IBAD buffer. The IBAD MgO texturing process is a nucleation process and the alignment occurs within a few nanometers instead of hundreds of nanometers in IBAD YSZ. Two parameters that greatly influence the quality of the textured IBAD – MgO films ($\Delta\phi = 8 - 9^\circ$) are the IBAD MgO thickness (10 nm) and the necessary substrate surface finish ($<1 \text{ nm } R_{\text{rms}}$) [54]. A LaMnO_3 (LMO) cap layer is typically grown epitaxially on top of the MgO to provide a good lattice – match with the superconductor films [55].

As described above, both the RABiTS and IBAD methods provide a biaxially – textured buffer which provide the foundation over which the HTS CCs are grown using different methods, which will be discussed later in the next section.

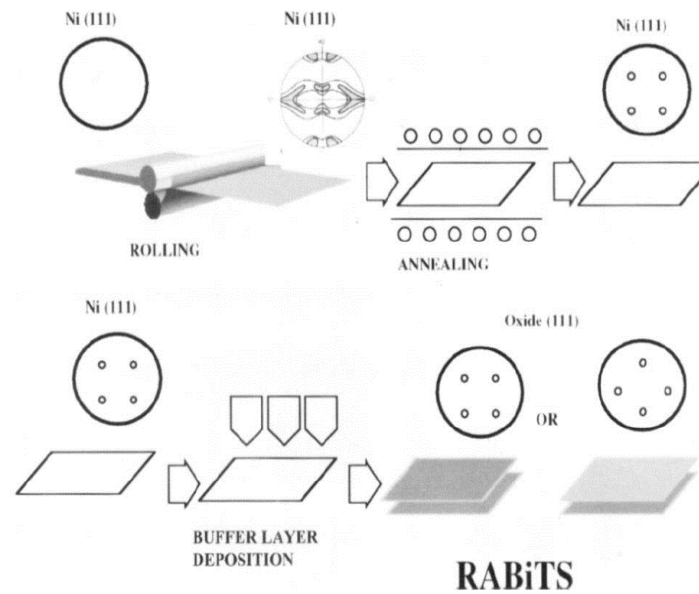


Figure 1.17 Schematic of the RABiTS technique and the crystallographic texture shown as pole figures obtained from X – ray diffraction.

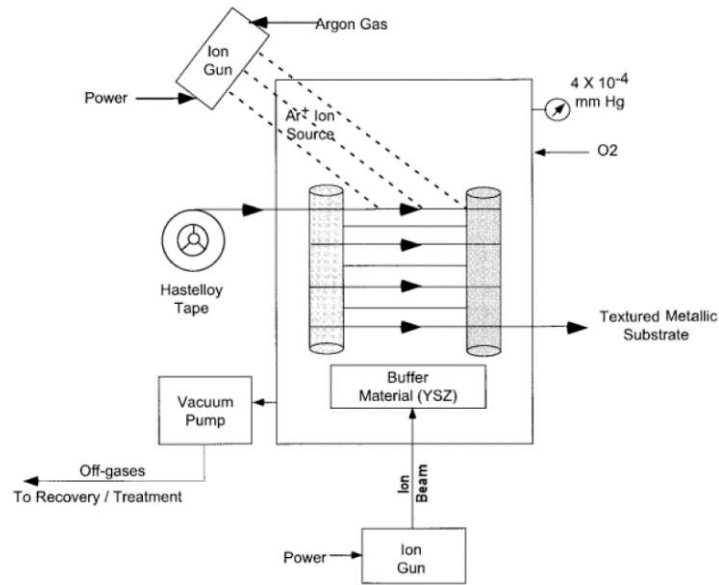


Figure 1.18 Schematic IBAD technique to grow biaxially-textured buffer layers of metal substrate.

1.9 YBCO Thin Film Growth

YBCO thin film growth falls into two major categories of physical and chemical methods.

- 1) **Physical Methods:** These include pulsed laser deposition (PLD), sputtering and reactive co – evaporation (RCE). These methods require expensive high vacuum systems and normally have a low deposition rate.
- 2) **Chemical Methods:** These include Metal Organic Chemical Vapor Deposition (MOCVD), Chemical Solution Deposition (CSD), Chemical Vapor Deposition (CVD), Metal Organic Deposition (MOD), and liquid phase epitaxy. These methods do not require expensive high vacuum systems and normally have a high deposition rate.

Coated conductors are commercially available from several manufacturers and their REBCO process methods are summarized in Table 1.4.

Table 1.4 REBCO process methods of different companies. [63].

Company	SuperPower	Fujikura	Bruker	SuNAM	American Superconductor
Process	IBAD	IBAD	IBAD	IBAD	RABiTS
Buffer Layer Deposition	Physical	Physical	Physical	Physical	Physical
REBCO Deposition	Chemical, MOCVD	Physical, PLD	Physical, PLD	Physical, RCE	Chemical, MOD

1.9.1 Pulsed Laser Deposition (PLD) Process

Pulsed Laser Deposition (PLD) is a thin film deposition method that belongs to the category of Physical Vapor Deposition (PVD). The target and the substrate are placed in a vacuum chamber in the PLD method. The material is ablated from the target surface due to the absorption of sufficiently high energy pulsed laser radiation focused on the target. The ablated material from the target surface is vaporized and expands perpendicular to the target surface, forming a plasma plume. A plasma plume consists of ions, molecules, electrons, atoms, particles and molten droplets. The plasma plume is then directed towards the heated substrate and condenses in the form of a thin film. A schematic illustration of the process is shown in Figure 1.19. Dijkkamp et al. [64] reported that short pulses and a short laser wavelength are required in order to minimize the spread of heat into the target. Normally, each laser pulse vaporizes or ablates a small amount of the material that is ejected from the target surface in a forward – directed plasma plume.

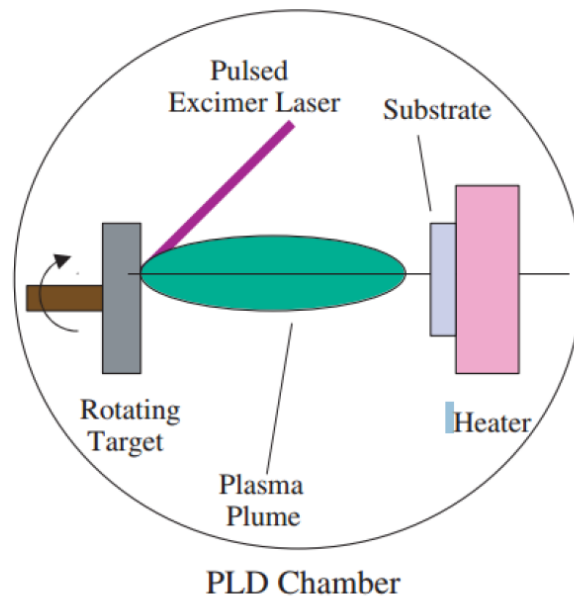


Figure 1.19 Schematic illustration of the PLD fabrication process.

1.9.2 Chemical Solution Deposition (CSD) Process

The Chemical Solution Deposition (CSD) method has various advantages such as high efficiency of precursor usage and a low cost non vacuum process. [65]. CSD starts with a homogeneous precursor solution containing metal ions, which is deposited on a substrate. The process is followed by a low temperature treatment (normally up to 600 °C) to dry and pyrolyze the organic compounds and a high temperature treatment (600 – 1200 °C) to crystallize the film in the desired oxide phase [66]. An overview of the CSD process is illustrated in Figure 1.20. The frequently used CSD processes are categorized, depending on the coating procedures, gelation of the deposited thin film and thermal annealing reactions into the following methods: [66].

- 1) Metal Organic Deposition (MOD).
- 2) Sol – gel method.
- 3) Hybrid routes using modifying ligands.

In the following section, the MOD process method used for the fabrication of YBCO thin films is discussed. American Superconductor Company (AMSC) uses a MOD method in its manufacturing line.

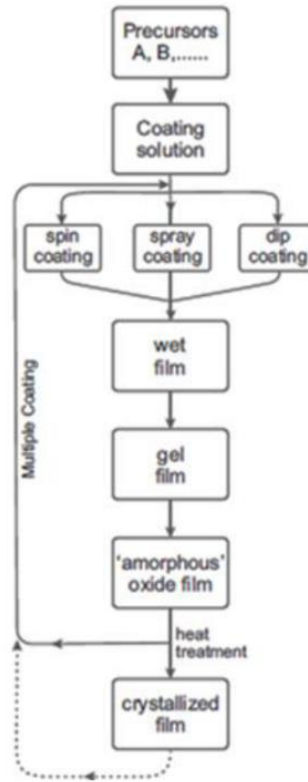


Figure 1.20 Overview of the typical chemical solution deposition process (CSD).

1.9.3 Metal Organic Deposition (MOD) solution synthesis

MOD is a CSD – based method. MOD method should meet certain minimum criteria, such as precursor stability in solvent, solution stability, substrate surface wetting, and minimal diffusion [67, 68]. In this method, the desired compounds are dissolved in a solvent in a specific ratio, based upon the desired composition of the final film. Conventional MOD methods use nitrates or carboxylates for YBCO thin film fabrication and results in rather low J_c at 77 K, 0 T (less than 1 MA cm^{-2}) due to the formation of BaCO_3 phase during the calcination process [69]. Gupta et al. [70] reported an alternative to the conventional MOD

method, based on the trifluoroacetate (TFA) precursor solution. In the TFA – MOD method, the acetate-based compounds of Y, Ba, and Cu are dissolved in trifluoroacetic acid and methanol, in a stoichiometric ratio. The formation of BaCO_3 can be avoided in the TFA – MOD method since fluorides are more stable than BaCO_3 . Once the film is coated onto the substrate in the TFA – MOD method, two heat treatment steps are performed. The first heat treatment step (heating up to 400 °C under moist oxygen gas flow), where metal trifluoroacetates are decomposed to oxyfluoride by the expulsion of carbon from the film, is also known as the pyrolysis step. The second heat treatment step, where the oxyfluoride film is heated to 800°C in the presence of a humid mixture of Ar^+ and 0.1% O_2 and followed by oxygen annealing at 450°C, is also known as the crystallization step [71]. Significant weight loss of the film during heat treatment processing, which can result in the cracks in the film, is one of the MOD processing challenges. Furthermore, it should be noted that this method has a very slow rate of crystallization. [72].

1.9.4 Metal Organic Chemical Vapor Deposition (MOCVD)

MOCVD is a popular chemical method for YBCO thin film growth. In the MOCVD deposition method, the precursor solution is delivered first to an evaporator. The vaporized precursor molecules are then carried to the MOCVD reactor by means of a carrier gas through a vapor delivery system where they then react to form the desired thin film on the heated substrate. A detailed illustration of the MOCVD process is provided in Chapter 2. MOCVD is an extremely versatile processing technique for large scale production of HTS CC, due to some of its salient features such as high deposition rates, large deposition area, large number of tunable process parameters and not being limited to line of sight deposition [73-77]. Berry et al. [78] reported the first growth of YBCO thin films by MOCVD on MgO substrate with a deposition rate of 8 nm min⁻¹. These YBCO thin films contained plenty of secondary phases and showed an onset critical transition temperature (T_c onset) of 75.1 K and a broad superconducting transition width (ΔT_c) of 38.8 K. Since then, there has been significant progress in the improvement of the MOCVD technique for the fabrication of YBCO thin

films. Currently, Superpower Inc. uses the MOCVD method to fabricate REBCO CCs.

Superpower demonstrated long length 2G HTS REBCO wire by reel to reel MOCVD with I_c of 200 A/cm in kilometer lengths and 300 A/cm in 600 m lengths in 2008 (Figure 1.21) [79].

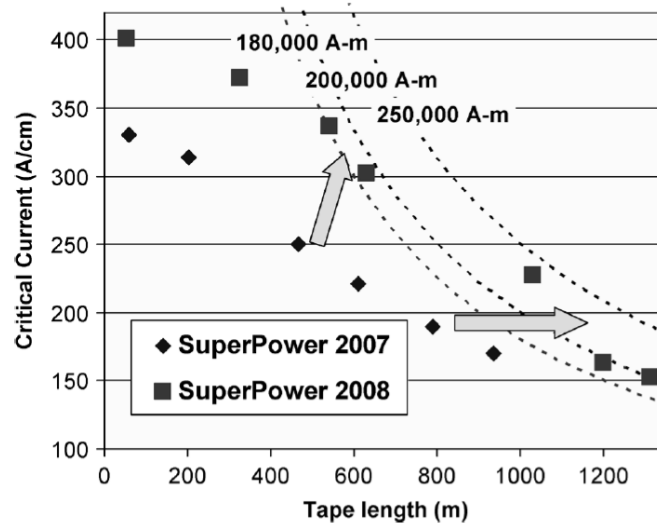


Figure 1.21 Long length 2G – HTS wire fabricated at Superpower Inc. Improved process conditions led to achievement of 200 +A/cm in kilometer lengths and 300 +A/cm in 600 m lengths in 2008[80].

1.9.5 Thickness dependence of critical current density

The obvious route to achieve high critical current (I_c) in REBCO CCs is to increase the film thickness. However, significant reductions of the critical current density (J_c) with increasing YBCO film thickness have been observed, as illustrated in Figure 1.22 [81,82]. The self-field J_c value at 75.5 K in YBCO film grown on single crystal substrate drops significantly from 8 MA cm⁻² to 3 MA cm⁻² within 1 μ m of film thickness (Figure 1.22(a)). The same behavior can be observed in Figure 1.22(b) in YBCO film grown on an IBAD – YSZ substrate. Foltyn et al [83] obtained a maximum I_c value of about 200 A/cm in 1 - 2 μ m YBCO film grown on IBAD – YSZ substrate, and observed that additional YBCO beyond the 2 μ m thickness resulted in reduced I_c . Normally, deposition of thicker YBCO films requires longer deposition time, thereby providing sufficient time for impurity diffusion from the substrate to contaminate the YBCO layer at the interface. Additionally, as the YBCO

thickness increases, the crystalline orientation can switch from c – axis to a – axis grains due to increasing thermal gradient in the direction perpendicular to the tape due to the insulating nature of thick YBCO layers. Moreover, decrease in J_c with increasing YBCO thickness can also be due to the film morphology becoming much rougher in thicker films [83].

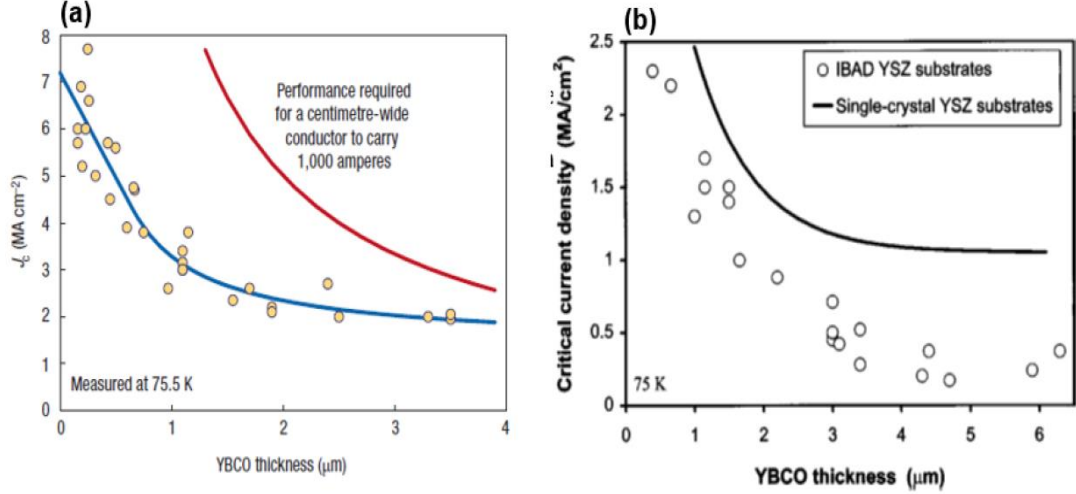


Figure 1.22 (a) Critical current density (J_c) dependence on YBCO thickness deposited on single crystal substrates [82]., (b) IBAD YSZ and single crystal YSZ substrates [83].

Recently, Majkic et al. [84] have demonstrated a method using an advanced MOCVD reactor to deposit 4.8 micron thick (Gd,Y)BaCuO tapes with 15 mol% Zr addition in single pass with record high critical current density (J_c) of 15.11 MA/cm² at 30 K , 3 T. Such record high performance in thick films (>1 micron) is a clear demonstration that growing thick REBCO films with high critical current density (J_c) is possible, contrary to the usual findings of strong J_c degradation with film thickness.

1.10 Artificial Pinning Centers in REBCO

Schematic views of the artificial pinning centers (APC) types based on the dimensions of the pinning centers in the YBCO films are shown in Figure 1.23. Random and correlated pinning centers produce opposite effects on the topology and dynamics of the vortex. Random pinning promotes entanglement, while the correlated pinning centers promote transverse

localization. The incorporation of Barium Zirconium Oxide (BZO) into YBCO thin films induced correlated pinning centers along c – axis. The strongest pinning is expected when the flux vortices are pinned by self-assembled columnar defects of sizes equal to the coherence length [27]. Mairov et al. [28] observed that the growth kinetics govern the microstructure of defects and that the best pinning mechanism is obtained with a mixture of self-assembled columnar defects and random nanoparticles. Based on their observation, the high I_c arises from a complex vortex pinning mechanism where self-assembled columnar defect generate large pinning energy, while nanoparticles and splay in columnar defects inhibit the detrimental flux creep effects.

Improvement in the in-field transport properties of the REBCO CCs is needed to meet the performance requirements for various commercial applications. This can be accomplished by using APCs with appropriate size, geometry, and density in to the REBCO thin films.

APCs are an effective approach for modifying the in-field I_c angular dependences of REBCO CCs. The in-field transport performance of REBCO films has been significantly enhanced by introducing APCs such as BaZrO_3 (BZO) [29–31], BaHfO_3 [34,35], BaSnO_3 (BSO) [36,37], Ba_2YNbO_6 (BYNO) [38], Y_2BaCuO_5 [39], and Gd_3TaO_7 [40]. Many studies have demonstrated that epitaxial BaZrO_3 (BZO) and BaSnO_3 (BSO) nanocolumns parallel to the REBCO c – axis, as well as the nanoparticles, are effective pinning centers.

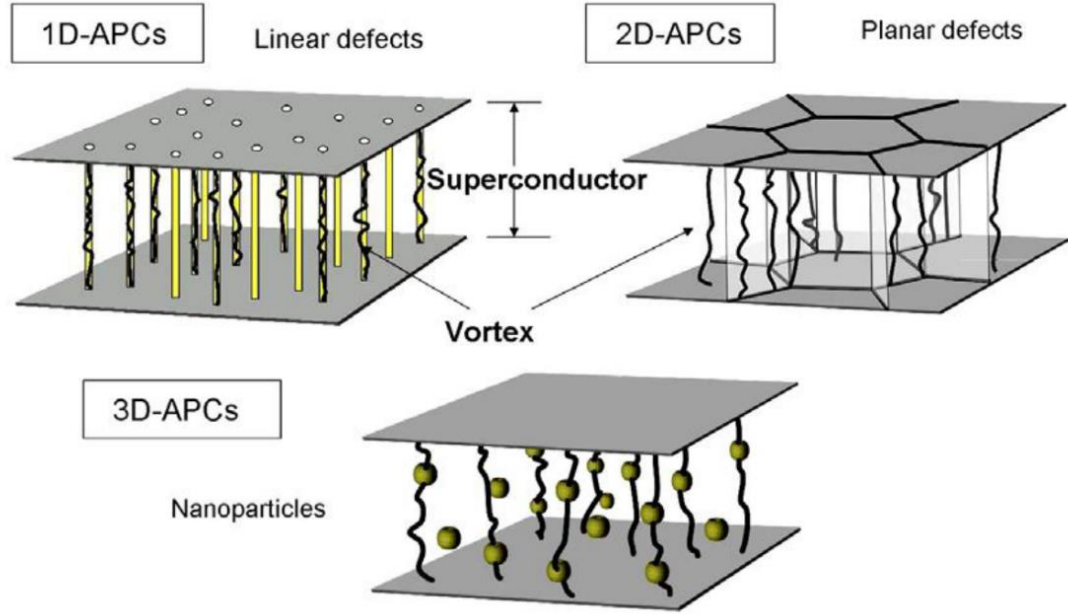


Figure 1.23 Schematic illustration of the dimensionality of artificial pinning centers [APC].

Efficient pinning occurs when the size of the defects is in the range of superconducting coherence length (ξ) which is approximately 2 – 4 nm at temperatures less than 77 K for YBCO and there is a high number density of defects on the order of $H/2 \times 10^{11} \text{ cm}^{-2}$, where H is the applied magnetic field [41,39].

McManus – Driscoll et al. [42] studied the effect of 5 mol % BZO in YBCO films grown by Pulsed Laser Deposition (PLD) on different substrates, and achieved J_c enhancements and strong pinning in magnetic fields parallel to the c – axis ($B||c$). Matsushita et al. [35] reported the improvement of in-field performance in 3.5 mol% BaHfO₃ (BHO)-added GdBaCuO grown by PLD on IBAD substrates and attributed it to the enhancement of the upper critical field (B_{c2}) coupled with reinforcement of flux pinning. Mele et al. [36] investigated the addition of BaSnO₃ (BSO) dopant (2 – 9 wt% range) to PLD processed YBCO films on SrTiO₃ (STO) single crystal substrates and achieved a pinning force of 28.3 GN m⁻³ at 77 K in 2 T with 4 wt% BSO addition.

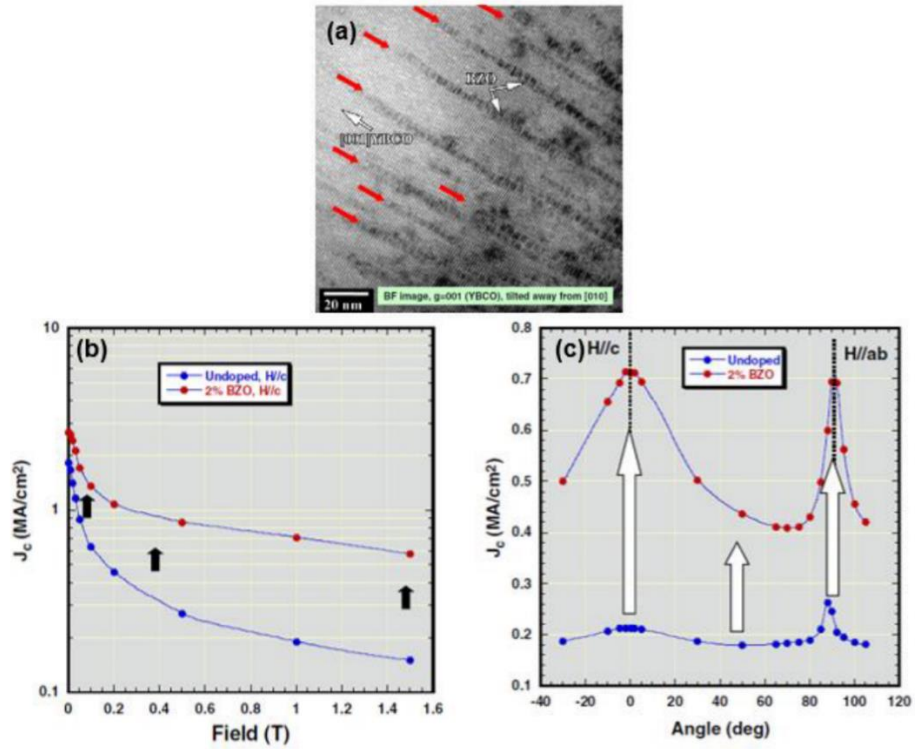


Figure 1.24 (a) TEM cross section of YBCO films with BZO deposited on flexible substrates by PLD. (b) Critical current density (J_c) as a function of applied magnetic field of an undoped YBCO film, compared to YBCO film with 2 vol% incorporated BZO (c) angular dependence of J_c at 77K, 1 T of an undoped YBCO film compared to YBCO film with 2 vol% incorporated BZO.

Goyal et al. [43] demonstrated that self-assembled BZO nanocolumns can be grown through the film thickness in YBCO doped with 2 vol % BZO (Figure 1.24(a)). A significant increase in J_c has been achieved when an applied magnetic field is perpendicular to the tape ($B \parallel c$) compared to an undoped sample. Figure 1.24(b) and Figure 1.24(c) show the magnetic field dependence of J_c and angular dependence of J_c at 77 K of those samples, respectively.

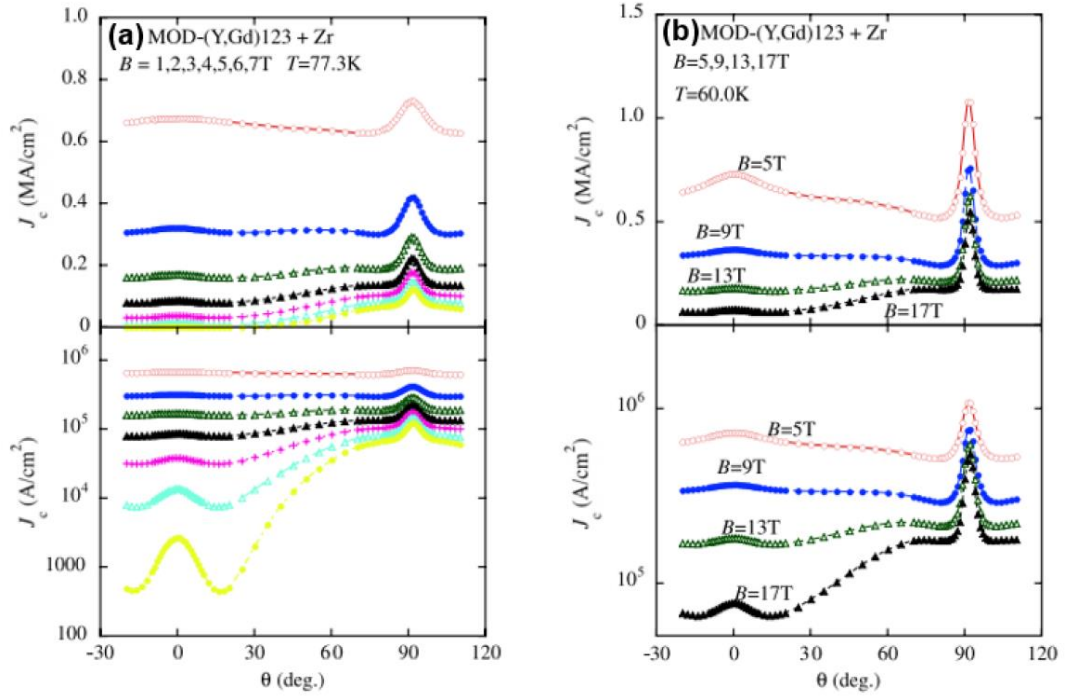


Figure 1.25 Angular dependence of J_c of (Gd,Y)BCO with 1 wt% of BZO grown by MOD in linear and log scales at (a) 77.3 K and (b) 60 K.

Three-dimensional (3D) nanoparticles dispersed in the superconducting film can drastically alter electromagnetic properties in a fashion that is quite distinct from those brought about by 1D and 2D APCs, due to the isotropic characteristics of nanoparticles. A critical current density with a nearly isotropic angular dependence at 77.3 K was reported by Awaji et al. [44] which is obtained by the introduction of 3D nanoparticles to the (Gd,Y)BCO coated conductors prepared by MOD. A nearly isotropic angular dependence of J_c can be seen in Figure 1.25(a) over a wide angular range except $\theta = 90^\circ$ ($B \perp c$). This behavior was dominant at low fields and is noticed to be suppressed as the field was increased. The flat angular J_c dependence is attributed to the strong randomly distributed pinning centers. The flat angular dependence of J_c disappeared when the temperature was lowered from 77 K to 60 K, as shown in Figure 1.25(b). When the temperature is lowered, the J_c peaks at $\theta = 0^\circ$ ($B \parallel c$) and $\theta = 90^\circ$ ($B \perp c$) both grew stronger.

1.11 Background and Motivation: Non Uniformity of superconducting properties along the length of REBCO tapes.

Commercial superconducting tape manufactured via MOCVD process has been known to show variations in the critical current density at 77 K, 0 T. Figure 1.26 is a graph showing Scanning Hall Probe Measurements (SHPM) of a commercial tape showing dropouts in a certain section. The dependence of the critical current density under the influence of magnetic fields at lower temperatures is further complicated due to variations in processing conditions of the MOCVD reactor with time which can lead to structural and chemical compositional variations along the length of the tape. Figure 1.27 is a measurement made using a custom 5 Tesla system showing variations in I_c along the length of commercial tape in a magnetic field.

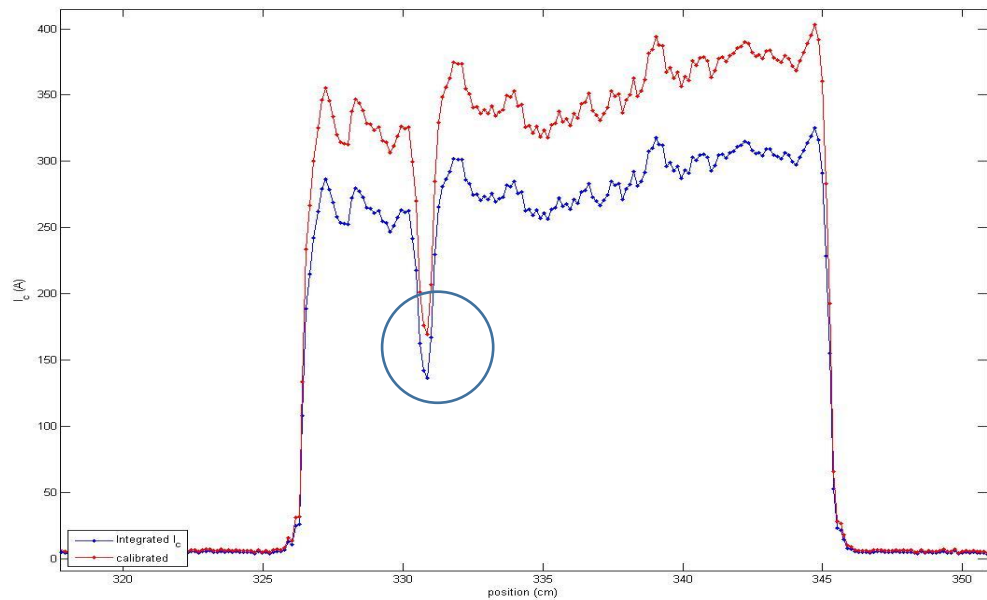


Figure 1.26 Scanning hall probe measurement of a commercial superconductor tape showing nearly 200 A dropout in critical current in the circled section.

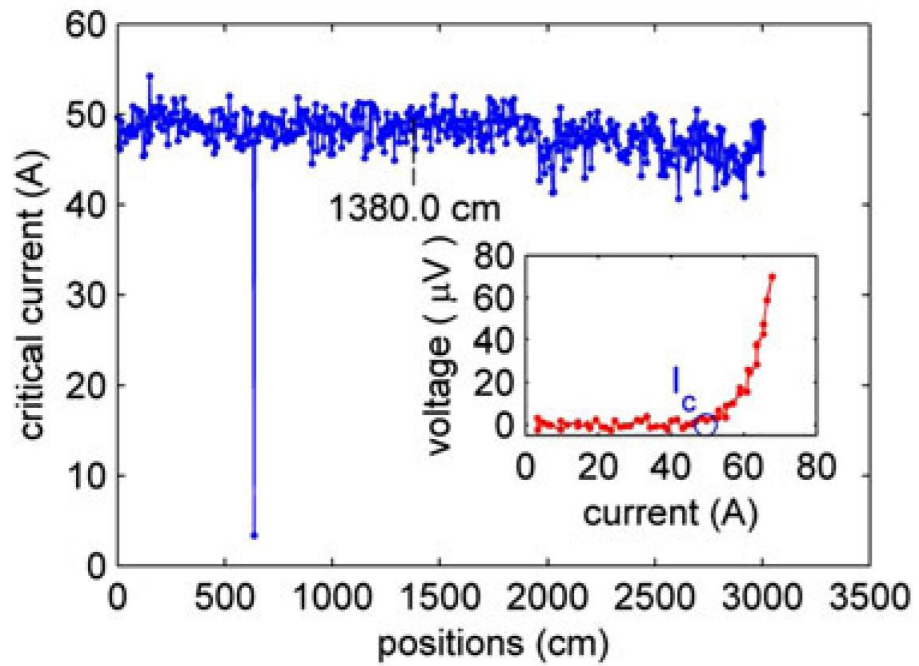


Figure 1.27 I_c measurement of a 30 m long coated conductor, at 77 K with 3 T field applied perpendicular to the tape surface. The inset is the $I - V$ curve measured at 1380.0 cm, which is randomly selected. The low I_c at 636 cm was a measurement artifact due to loose voltage contacts.[87]

Substantial reduction in I_c might be attributed to actual physical defects on the buffer tape or mechanical damage to the section. However, if such defects arose due to processing condition changes within the reactor over time, inline monitoring tools capable of pinpointing defective sections and potentially providing a corrective feedback signal to processing parameters in order to restore tape characteristics to nominal values, will prove to be invaluable especially for manufacturing superconducting tapes.

Non-uniformity of REBCO CCs might be due to structural variations in the physical properties of the REBCO crystals that are grown due to temperature or flow inhomogeneities within the MOCVD reactor. They can also result from chemical compositional variations in the vapor stream of the MOCVD process due to compositional gradients or inhomogeneous decomposition of precursor molecules. For the purposes of studying the structural properties, X-ray diffraction has been used as an in-situ, real-time measurement capable of monitoring

tape quality along the length in a non-destructive fashion. A custom-built system inline in the pilot MOCVD system was used in this study.

Heydari Gharahcheshmeh et al. [85] report that the critical current of Zr-added REBCO tapes is well correlated with the value of c – axis lattice parameter of the REBCO crystal. Both transport and magnetic critical current density (J_c) values at 77 K, self-field, as a function of REBCO c – axis lattice parameter are shown in Figure 1.28. The magnetic J_c values were obtained using Physical Property Measurement Systems (PPMS) measurements and show the same trend as the transport J_c values with respect to REBCO c – axis lattice parameter, although different in absolute terms. This difference can be ascribed to a stricter criterion of PPMS measurement, which is several orders of magnitude more rigorous than the usual transport current criterion of $1 \mu\text{V cm}^{-1}$ [86].

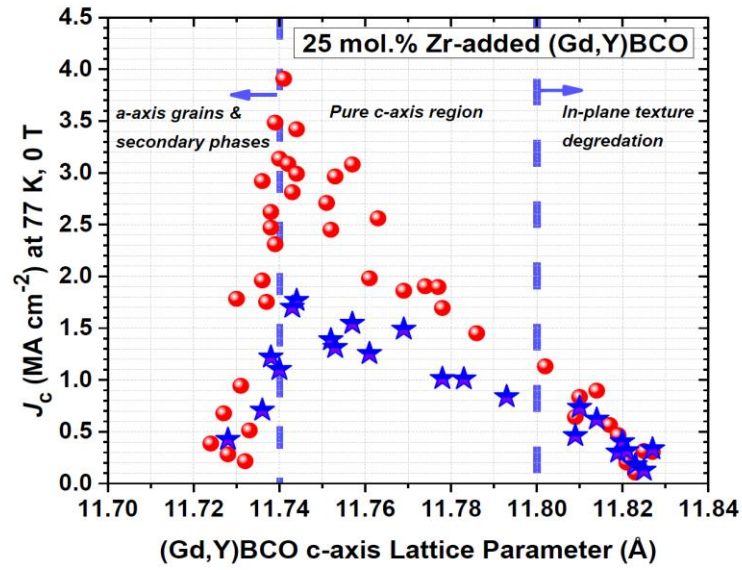


Figure 1.28 Transport (red – colored circles) and magnetic (blue – colored stars) J_c values at 77K, 0T as a function of (Gd,Y)BCO c – axis lattice parameter of 25 mol% Zr – added (Gd,Y)BCO superconductor tapes [90].

The Zr content of the final deposited film was found to vary in a small range - between 2.8 at% and 3.4% as determined from Inductively Coupled Plasma – Mass Spectroscopy (ICP – MS) analysis in 25 mol% Zr – added REBCO superconductor tapes. Even within this narrow range, the Ba/Cu content plays an important role in the variation of

REBCO c – axis lattice parameter as shown in Figure 1.29. In general, it can be concluded that the REBCO c – axis lattice parameter strongly depends on the Ba/Cu content of REBCO superconductor tapes with the same BZO volume fraction. It is postulated that as REBCO superconductor tapes become more Ba – rich, the excess Ba content occupies the yttrium (Y) sites and due to the high ionic radius of Ba in comparison with Y, the REBCO c – axis lattice parameter expands. McManus – Driscoll et al. [88] reported approximately 14 % Ba and Y cation exchange in heavily disordered YBCO films, using Rietveld refinements of X-ray diffraction data.

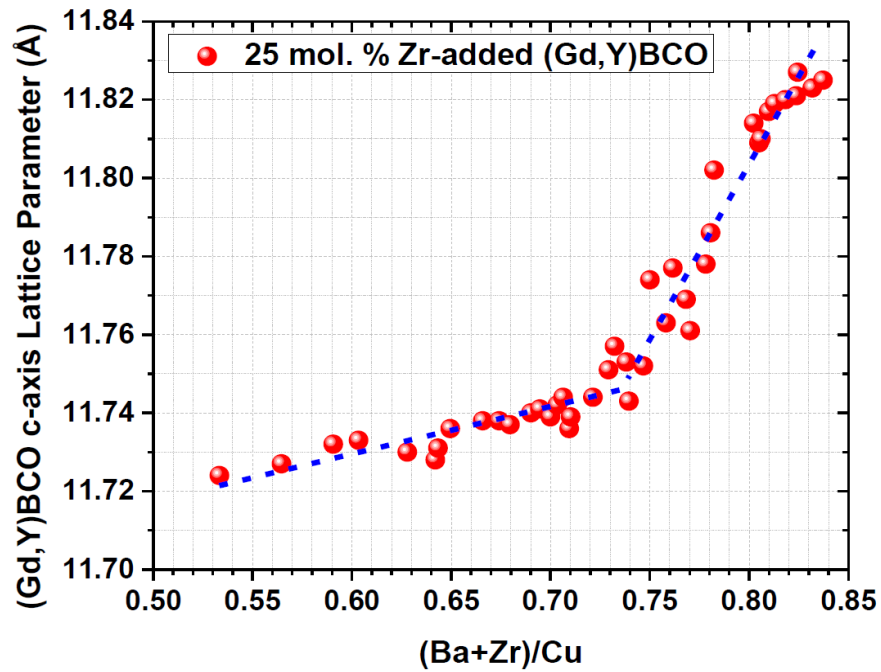


Figure 1.29 REBCO c – axis lattice parameter of forty-two 25 mol% Zr – added REBCO superconductor tapes as a function of (Ba+Zr)/Cu content. The dashed lines are guides to the eye. [85].

It has been shown by Wu et al.[89] that the strain fields developed around BZO nanodots embedded in the REBCO matrix is a key driving force dictating the self-assembly of BZO nanodots along the REBCO c – axis in the form of well-oriented nanocolumns. Lattice mismatches in the range of 5 – 12 % generate adequate local strain fields required for the self-assembly by Strain Propagated Self-Assembly mechanism [SPSA] [89]. Table 1.5 shows that

the mismatch between the lattice parameters of the embedded secondary BZO phase and the primary REBCO phase falls within this regime, which provides impetus for this mechanism to occur provided the processing conditions during MOCVD are suitable.

Table 1.5 Lattice mismatch for BZO pinning dopants with respect to REBCO along three crystallographic directions. The [003] mismatch is also shown since $c/3$ of the orthohombic YBCO provides a closer match with the cubic lattice of the dopants.

Lattice Direction	[100]	[010]	average a and b	[003]
BZO	8.85%	7.25%	8.05%	7.08%

It has been shown by Selvamanickam et al. [90] that the high lift factor samples consist of well-aligned BZO nanocolumns continuous from the buffer layers to the film surface. Figure 1.30 is a cross sectional TEM image comparing a low lift factor sample to a high lift factor sample, the latter showing excellent nanorod alignment perpendicular to the tape substrate. Well-aligned BZnanorod engineering is an essential prerequisite for manufacturing tapes with good in-field properties.

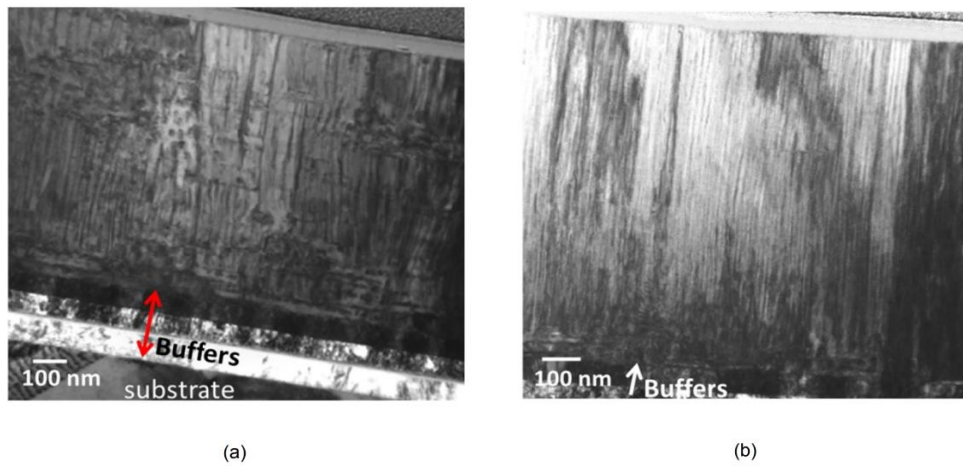


Figure 1.30 Cross sectional microstructures of $0.9\ \mu\text{m}$ thick, Zr doped REBCO tapes with same J_c @77 K, 0 T but with (a) Low lift factor and (b) high lift factor at 30 K, 2.5 T. [90]

By monitoring subtle shifts in the lattice parameter of the superconducting crystals with well-aligned nanorods using inline XRD, it might be possible to develop a novel quality-

monitoring tool that is capable of tracking *in-situ* variations in nanorod alignment and predicting downstream performance.

2D GADDS XRD has also been shown to be a useful tool in determining the physical structure of primary as well as secondary phases in a given material. The thicker REBCO tapes made by Advanced Metal Organic Chemical Vapor Deposition system (AMOCVD) exhibit excellent in-field magnetic critical current density thanks to higher nanorod density per unit area of the tape. Certain unique characteristics have been observed using 2D GADDS XRD in tapes that show excellent magnetic in-field performance. Fig 1.31 is a comparison of the XRD pattern obtained from 2D GADDS between two tapes – one with low lift factor and the other with high lift factor.

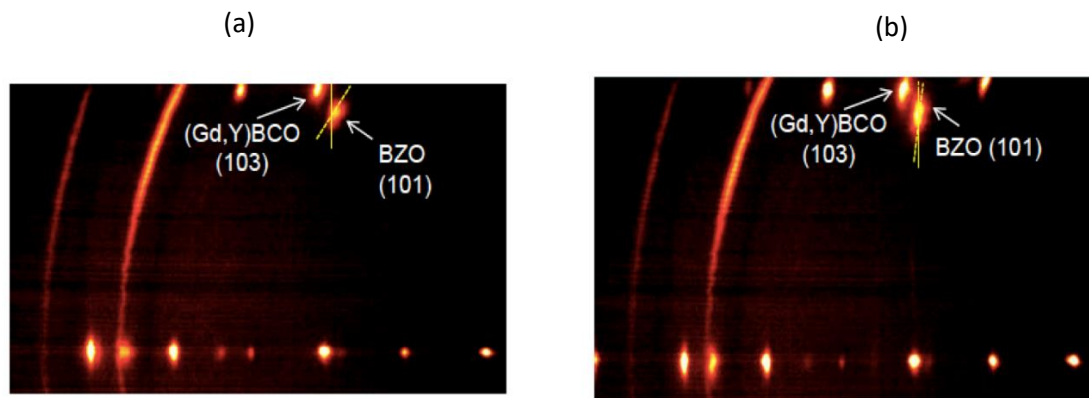


Figure 1.31 2D GADDS XRD pattern of (a) Low lift factor tape, (b) High lift factor tape.

It is observed that tapes with low lift factor have the BZO (101) peak streaking in the direction of constant 2θ as opposed to tapes with high lift factors which have the BZO (101) peak streaking almost perpendicular to the direction of constant 2θ . The streaking angle can be geometrically defined as shown in Figure 1.32.

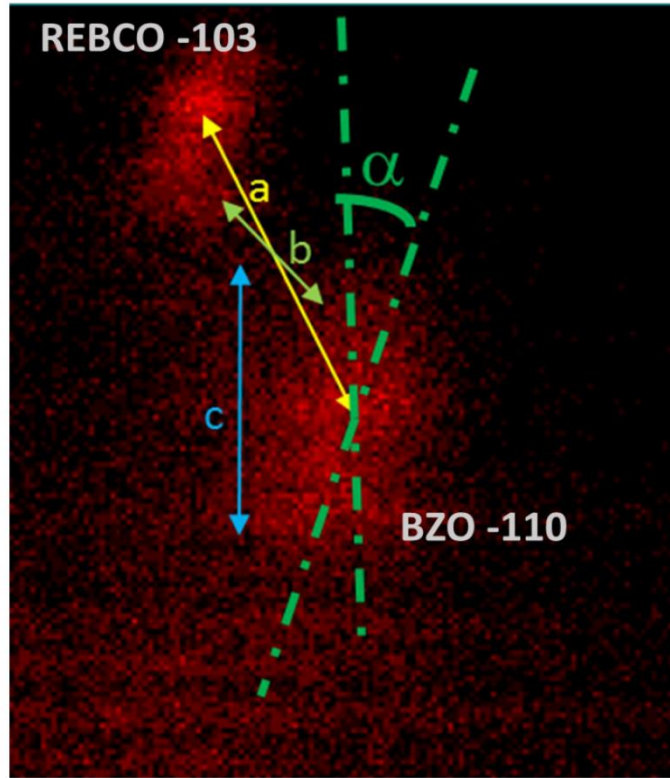


Figure 1.32 Geometrical construction for determination of streaking angle of (110) BZO peak.

In Figure 1.32, the angular deviation of the BZO (110) peak from the normal drawn to it is defined as streaking angle α . This streaking angle, which is arising in the 2D GADDS XRD because of the physical dimensions of the nanorod, has been correlated to important properties like magnetic in-field critical current of the tape. Figure 1.33 – Figure 1.35 show some of the correlations that have been established between this angle and chemical compositional variations and critical current and lift factor of the thicker REBCO films at 4.2 K, 13 T.

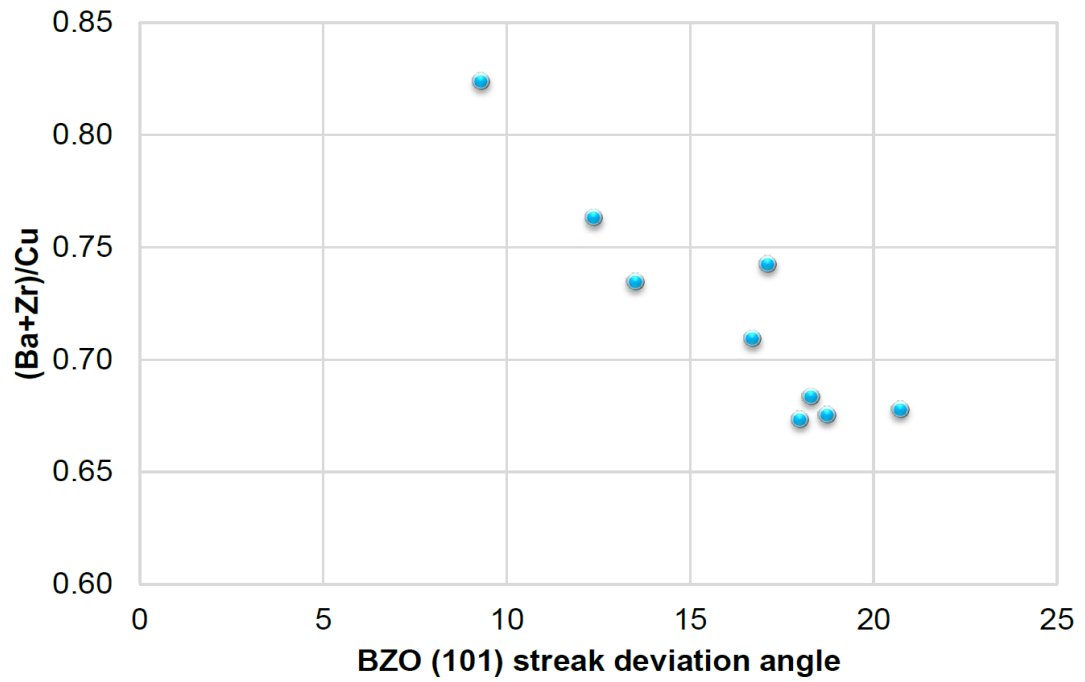


Figure 1.33 (Ba+Cu)/Zr vs BZO (101) Streak deviation angle.

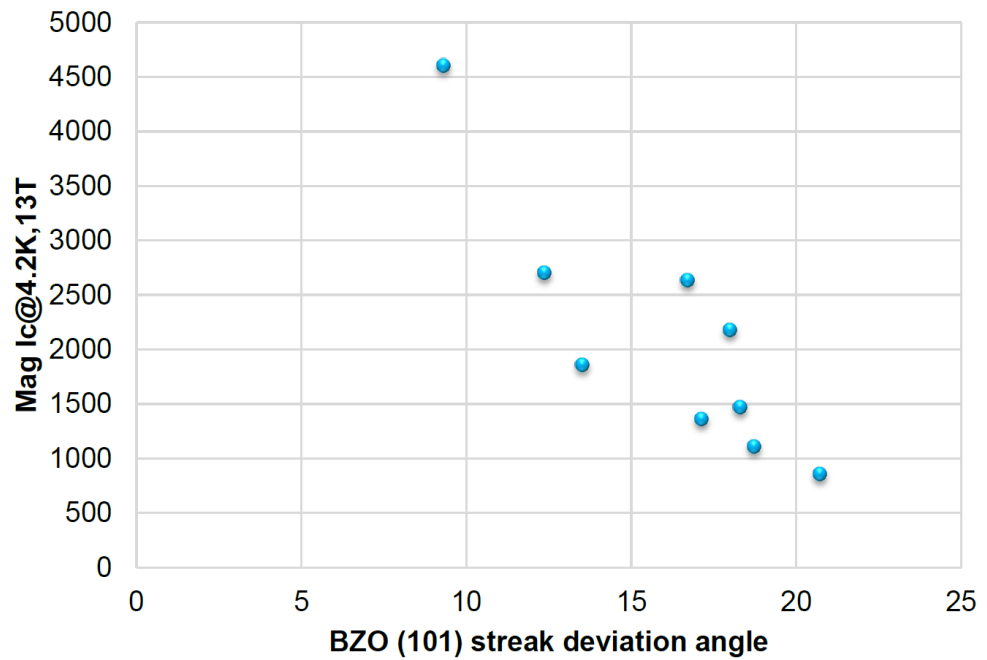


Figure 1.34 Magnetization I_c at 4.2 K, 13 T vs BZO (101) Streak deviation angle.

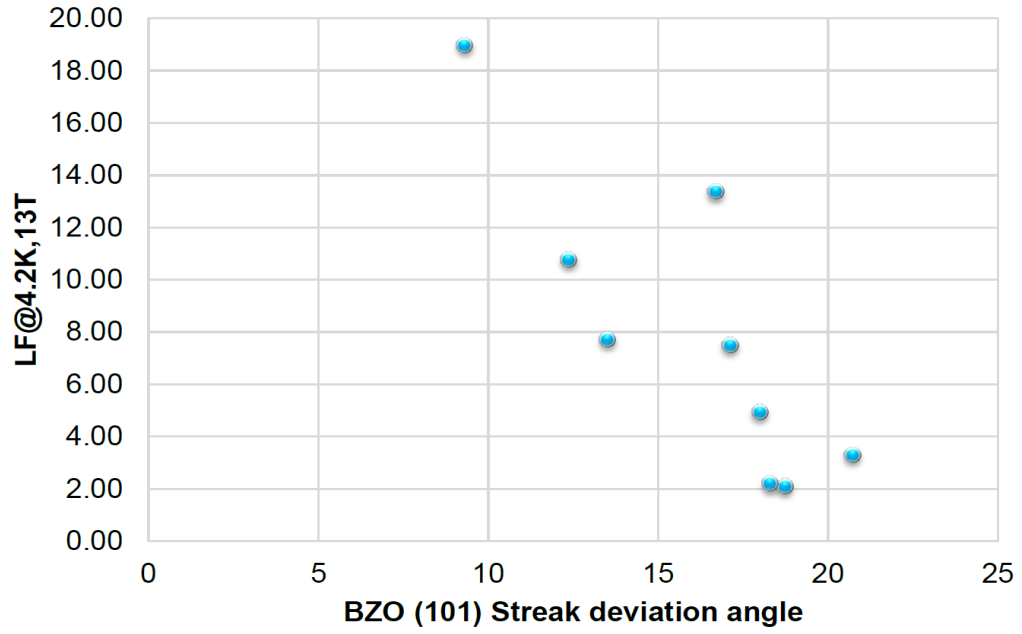


Figure 1.35 Lift factor at 4.2K, 13 T vs BZO (101) Streak deviation angle

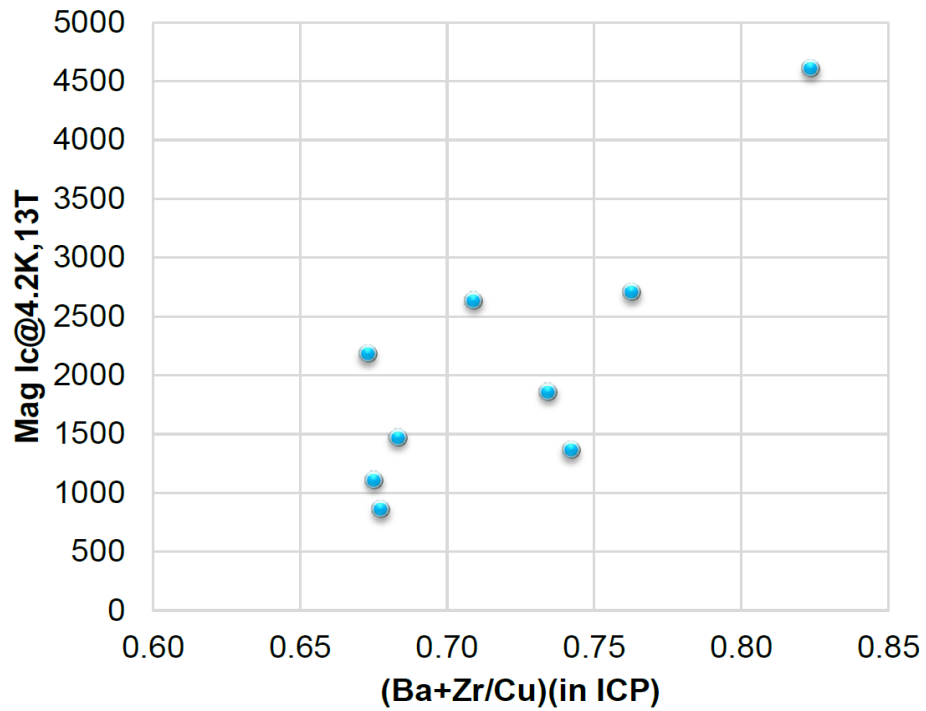


Figure 1.36 Magnetic I_c at 4.2 K, 13 T vs (Ba+Zr)/Cu

It can be clearly inferred from Figure 1.33 – Figure 1.35 that the streak deviation angle observed in the BZO (110) peak in the 2D GADDS XRD can be correlated with important magnetic field performance parameters and chemical compositional variations in

the REBCO thick films. Tracking this parameter in real time could provide invaluable information about the quality of tape performance downstream and this data could potentially be used as corrective feedback mechanism to adjust process parameters to maintain nominal tape characteristics.

UV absorption spectroscopy has already been demonstrated as a tool capable of monitoring variations in the chemical composition of precursor molecules used in MOCVD deposition of REBCO thin films. [91]. Figure 1.37 is a schematic of the assembly system with a switcher circuit for monitoring the concentration of bubbler output of individual elements for real-time monitoring using UV absorption spectroscopy. UV visible spectrum is conventionally used for quantitative analysis of known precursor molecules. This makes it more suitable for single output bubbler architecture but not useful for analyzing complex multi-gas mixtures. FTIR is a superior option as a qualitative technique capable of identifying multi-gas mixture rapidly by generating a unique vibration spectrum for each molecule which renders it more suitable for the evaporator architecture where a cocktail of precursor solution is used in the vapor lines. Figure 1.38 illustrates a feedback control mechanism using UV absorption spectroscopy to vary the amount of carrier gas fed into the bubbler with a MFC to control the output of a specific bubbler.

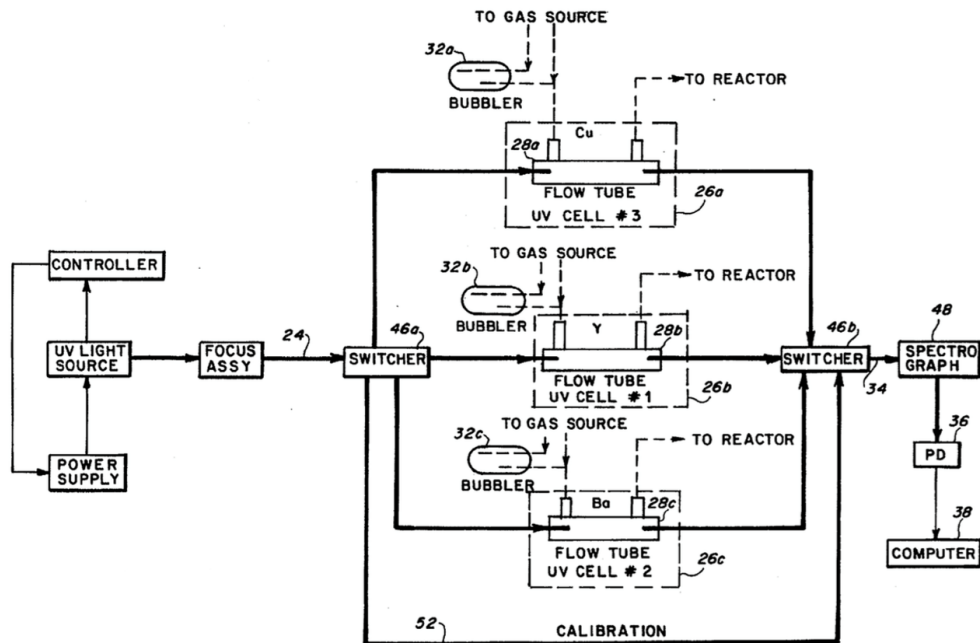


Figure 1.37 Schematic of inline UV absorption spectroscopy with switcher circuit for YBCO film growth. [91]

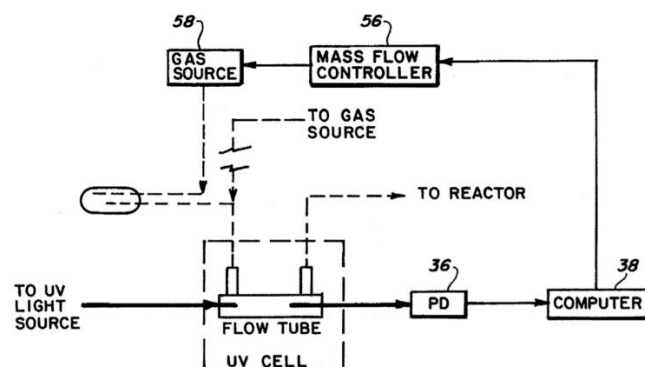


FIG. 5

Figure 1.38 Schematic of feedback control of bubbler output using MFC to manipulate carrier gas output to the bubbler as a function of concentration measured by UV absorption spectrometer. [91]

In situ FTIR studies have also been demonstrated as a viable route to study the decomposition of REBCO precursor molecules at the elevated temperatures of deposition inside the MOCVD reactor. Figure 1.39 is a schematic of setup used by Kovalgin et al. [92].

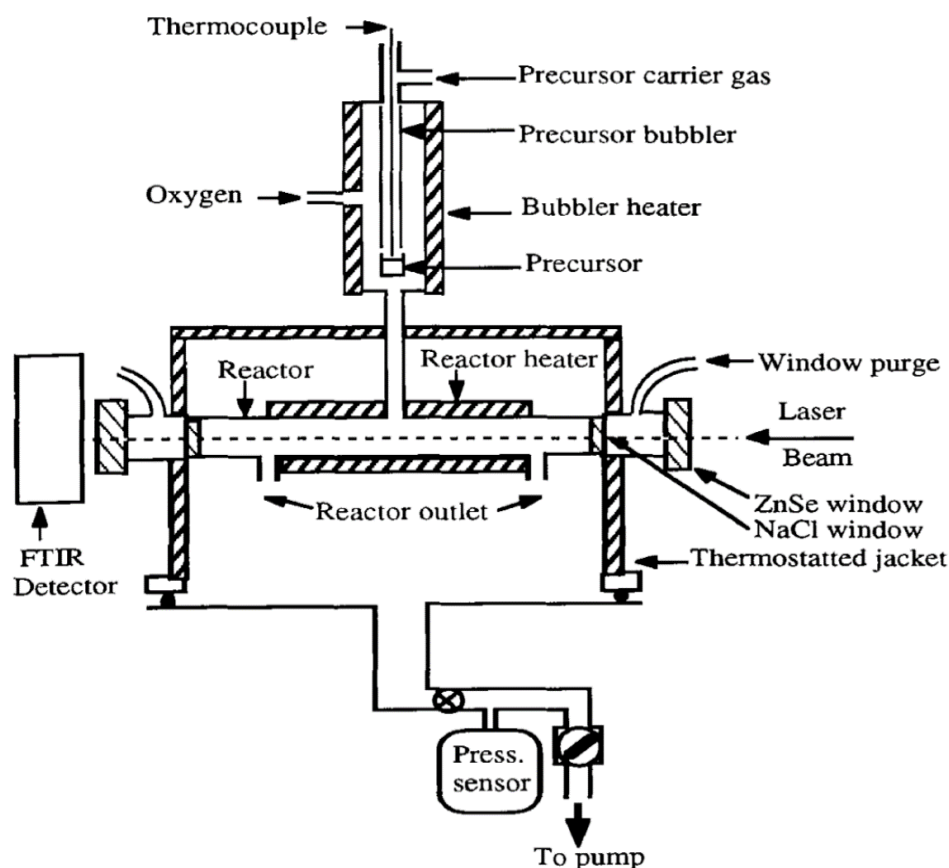


Figure 1.39 Schematic of the setup used by Kovalgin et al. to study *in situ* decomposition of individual precursor molecules inside the MOCVD reactor for growing YBCO in thin films [92].

But *in situ* accessibility of vapor stream to FTIR instrumentation in the current generation of AMOCVD reactors that are being developed is very limited since the laminar flow architecture keeps the vapor stream enclosed in a tight volume with no viewports for IR signals to penetrate into the reaction zone. A more novel approach would be to sample the vapor stream at the output of the MOCVD evaporator using a sampling device that can be integrated into the vapor path assembly seamlessly. FTIR is a powerful tool capable of analyzing multi-gas mixtures in real time and providing a fast output signal that can be

integrated into a control loop whereby the concentration of individual precursor elements at the output of the evaporator can be controlled by varying the injection rates of individual metalorganic compounds to the evaporator. Different thermal stabilities of metal organic compounds in vapor phase result in a noticeable difference in film to precursor composition ratio in REBCO films grown by MOCVD [93]. Although this technique cannot address chemical compositional inhomogeneity due to variations within the reaction zone inside the MOCVD reactor, this is a first step towards ensuring chemical homogeneity of the precursor molecules that are delivered from the evaporator to the reactor.

Chapter 2

2.1 Experimental Methodologies

This section presents a detailed description of the reel-to-reel Metal Organic Chemical Vapor Deposition System (MOCVD) and its operating procedures including liquid precursor preparation and buffer tape preparation process involved in the fabrication of REBCO coated conductors. Both the first generation system ('M1') and the advanced MOCVD reactor (A-MOCVD – 'PM') system that were utilized in fabricating the tapes measured in this study will be described. The post processing steps that are usually involved after the growth of the REBCO film in the MOCVD reactor including silver sputter deposition and oxygenation annealing process are also discussed. Finally, the electromagnetic testing and materials characterization methods used for REBCO conductors are illustrated.

2.1.1. Metal Organic Chemical Vapor Deposition System (MOCVD)

All the REBCO films that were measured using the simple 1 – D detector inline X-ray Diffraction (XRD) system were made with the M1 system. This is a cold wall, reel to reel MOCVD system that is shown in Fig. 2.1. A liquid precursor solution is injected to the evaporator by a liquid pump while the flow rate of the precursor delivery is controlled at a constant rate of 2.5 ml/min. The output rate of the metering pumps is adjusted by controlling the stroke volume and/or altering the RPM of the rotating piston in the cylinder liner by using an electronic controller.

There are two pneumatic valves in the delivery line and the vaporized precursor can either be directed towards the MOCVD reactor or by passed to the vacuum pump by switching on or off the valves. The vaporized precursor was delivered to the MOCVD reactor with a carrier gas of Ar. All gas flows in both the evaporator and MOCVD reactor are

controlled by means of Mass Flow Controllers (MFC). Just before entering the reactor, the vaporized precursor molecules are mixed with heated oxygen gas preheated to about 185°C. The molecules get dispersed through two sections of the showerhead consisting of a dispersion plate and a faceplate before reaching the susceptor region. Upon reaching the heated tape on top of the susceptor, the molecules have enough thermal activation energy to disintegrate and react to form the REBCO thin film on the tape. The showerhead is maintained at a temperature of about 285 °C and has vapor guides installed around it to control the dispersion of the vapors. The temperature of the showerhead is monitored and controlled by using an OMEGA CN3000 microprocessor temperature controller which is connected to the cooling water HPLC pump Model 426.

An Inconel susceptor was used in this research work. The movement of the tape on the susceptor was controlled at a constant speed of approximately 2.1 cm/min with a sufficiently applied tension on the tape using a torque motor. The applied tension on the tape ensures uniform heat transfer by making firm physical contact with the susceptor. A spool of buffered substrate to be processed is positioned in the dispense side of the reactor. A blank spool is placed on the take up side of the MOCVD reactor where the tape is wound up after REBCO deposition. The temperature of the susceptor is maintained at approximately 955 – 985°C. A total of 13 halogen lamps placed in seven zones are used as heating elements for the susceptor.

A dry vacuum pump is used to keep the evaporator and reactor under vacuum. The pressure of the MOCVD reactor was maintained at 2.3 Torr during the deposition by a pneumatic throttle valve which is located between the reactor and the vacuum pump. The exhaust vapors from MOCVD reactors are filtered before being exhausted through the vacuum pumps. The residual oxygen concentration in the MOCVD reactor was monitored by using an oxygen sensor.

Type K thermocouples (Chromel – Alumel) were used to monitor the temperatures of the vapor path sections at different points. The positions of the thermocouples are shown in

Fig 2.1(a). The temperature of the delivery line from the evaporator to the MOCVD reactor is maintained and controlled within a window of 265 – 295 °C in order to prevent condensation or decomposition of the vaporized organic compounds before they reach the substrate. Each section of the MOCVD system is heated with different heating tape configurations which are connected to variacs that help control the power output given to each tape.

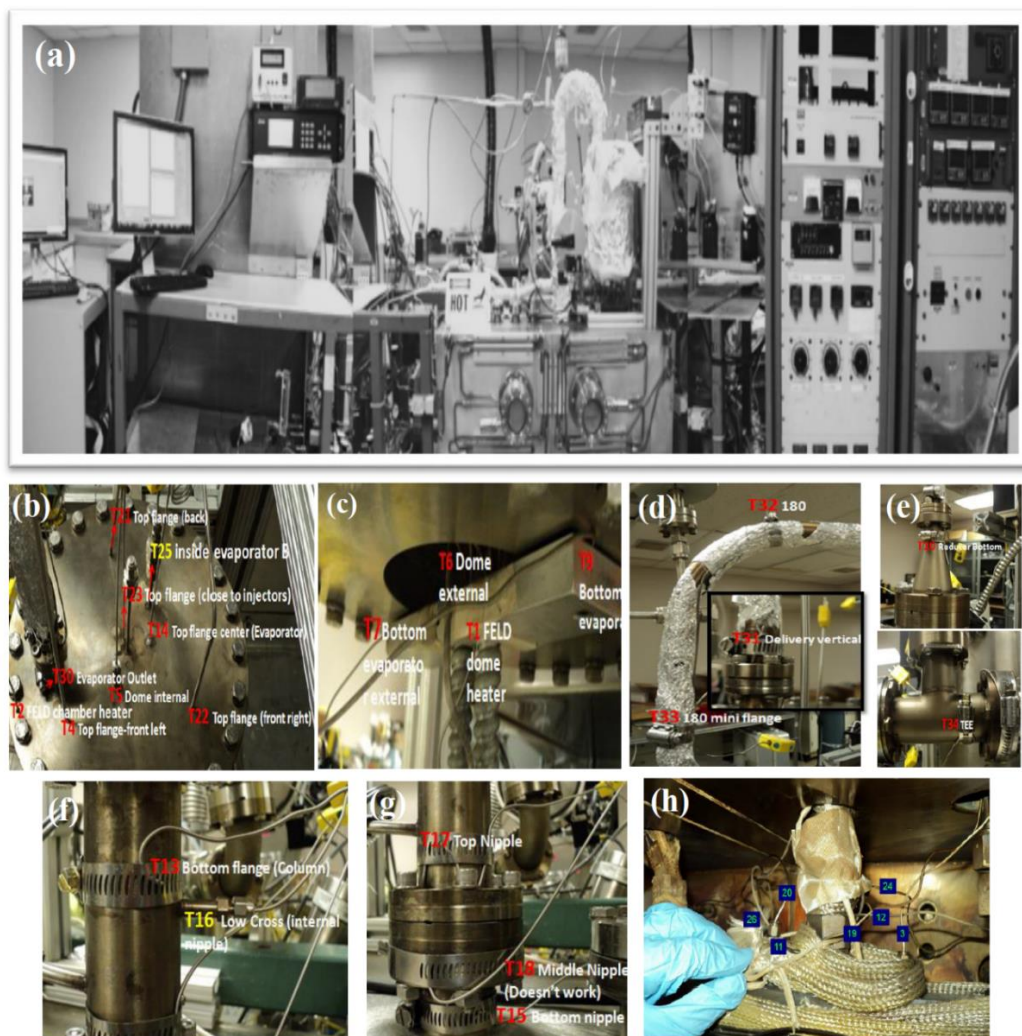


Figure 2.1 Reel to Reel MOCVD system used in this research work. (a) Locations of the K – type thermocouples which are used to monitor and control the vapor temperatures at different points inside the evaporator, (b) bottom section of evaporator, (c) delivery line, (d) reducer and tee sections, (e) bottom flange, (f) Bottom flange connected to chamber, (g) Nipple section connecting atmosphere to inside of vacuum chamber (h) showerhead.

After deposition of the last sample, THF is flowed for a while to clean the injector and delivery lines. The heating source of the showerhead as well as the susceptor is turned off after stopping the THF flow. Finally, the bypass valve is opened to place the evaporator under vacuum when the system is not in use while the reactor valve is closed. Once the susceptor is cooled down, the chamber can be opened after purging and the deposited tape spool is removed for post processing which will be discussed in sections 2.2 and 2.3. A deposition rate of approximately 80 nm min^{-1} was used and the tape speed was controlled to produce REBCO films with thickness of about $0.9 \text{ }\mu\text{m}$. A schematic of the MOCVD system is illustrated in Fig 2.2

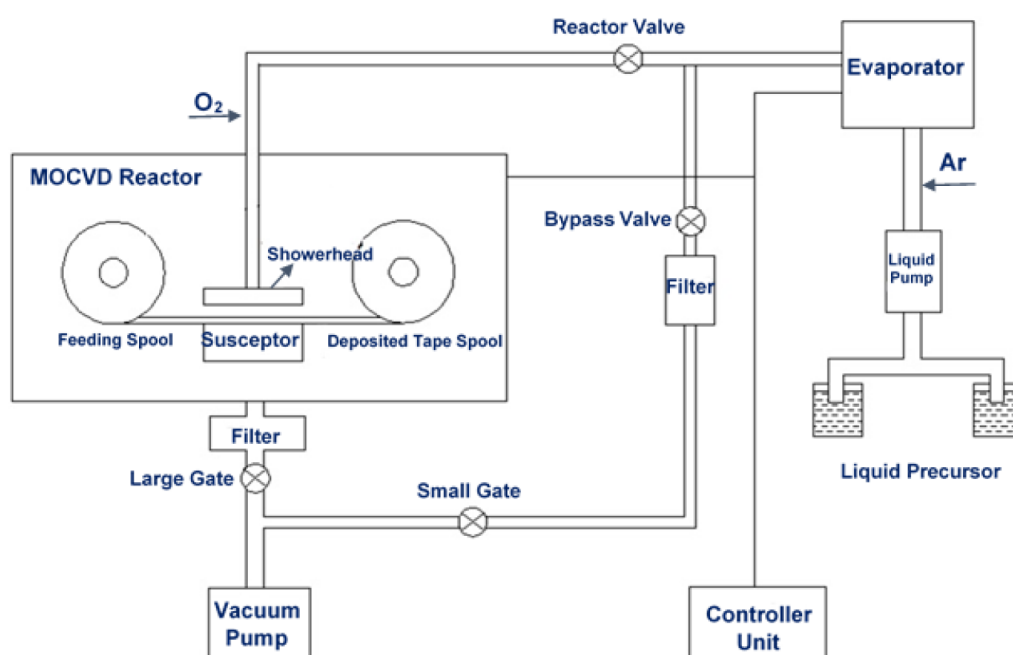


Figure 2.2 Schematic illustration of the Reel to Reel MOCVD system.

2.1.2. Advanced - Metal Organic Chemical Vapor Deposition System (A -MOCVD)

The second part of the study includes tapes that were prepared in the newer Advanced – MOCVD systems (AMOCVD). The fundamental drive towards the development of this newer, advanced system was to address the shortcomings of the previous generation of technology particularly in the production of thicker tapes. Susceptor contact heating has certain limitations such as poor temperature control and non-uniformity of temperature profile of the susceptor with degradation due to oxide deposition over time. Moreover, the showerhead flow pattern was deemed to be too turbulent and non-uniform which further leads to temperature gradients within the reaction zone. With all this in mind, a completely new system was designed with the fundamental idea of heating of the substrate by virtue of its resistance and maintaining uniform laminar flow with a parallel plate design. Figure 2.3 shows a schematic of this system. The second part of this study with 2D General Area Detector System (GADDS) inline XRD primarily involves the investigation of these thicker tapes with the aim of finding potential correlations between the critical current at 77 K, in field performance and structural variations that can be tracked using 2D GADDS XRD in real time.

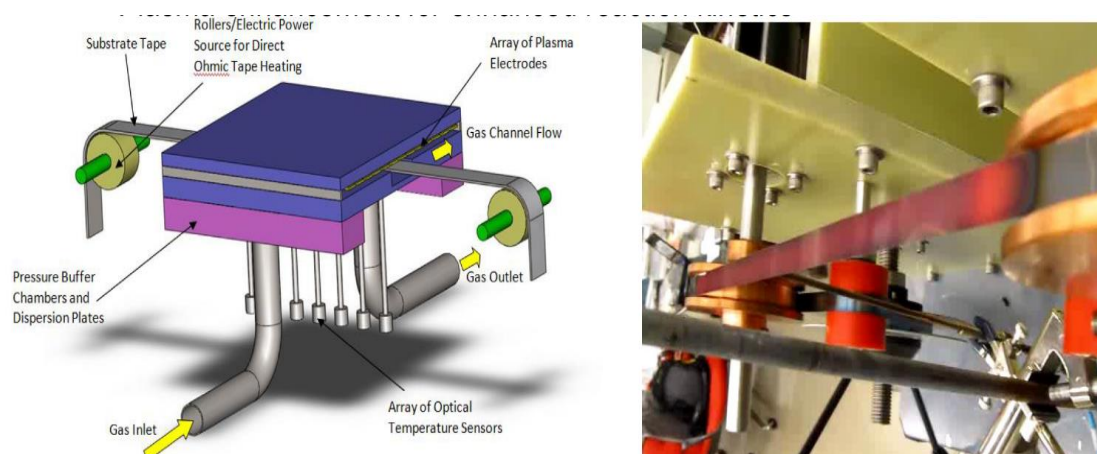


Figure 2.3 Schematic of Advanced MOCVD system. Picture on the right shows the concept of direct heating with rollers.

2.1.3. Liquid Precursor Preparation

The precursor solution was made by mixing the tetramethyl heptanedionate (thd:2,2,6,6 – Tetramethyl – 3,5 – heptanedionate) compounds of Zr, Gd, Y, Ba and Cu in tetrahydrofuran (THF) solvent in the appropriate mole ratios. All these compounds are in powder form and are purchased from Sigma Aldrich. Each compound is weighed based on a prepared recipe with a precision of 0.0001 g and the calculations of the exact mass of each element is performed based on the molar concentration. Zr metal organic compound, which is added as a dopant, is not included in the calculation of the total molar value of the other compounds. Zr is added as 5, 15 or 25 % of the total molar value of the other elements in the precursor solution. The prepared precursor solution is magnetically stirred for at least 2 hours to ensure that all the compounds are homogeneously dissolved in the solvent. THF has a tendency to decompose under the influence of heat or light, so the solutions are prepared in amber bottles to avoid direct exposure to light for extended periods of time.

2.1.4. Buffer Tape Preparation

REBCO coated conductors were fabricated on a Hastelloy C – 276 (12 mm width and 50 μm thickness) with Biaxially textured IBAD – MgO template and a LaMnO₃ cap layer. The schematic illustration of the all the buffer layers involved in REBCO coated conductors is shown in Figure 2.4.

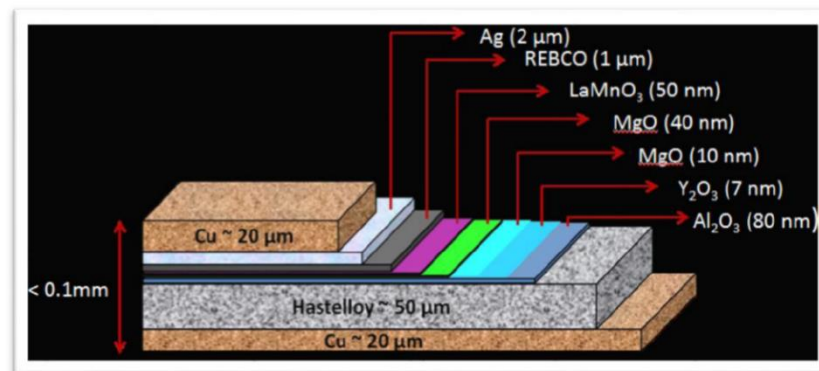


Figure 2.4 Schematic illustration of the buffer layers used in REBCO coated conductors.

A brief description of all the layers used in the architecture of REBCO coated conductors is given below:

- 1) Hastelloy C – 276: A nickel based superalloy with elemental composition by weight percentage as 55.06% Ni, 16% Cr, 16% Mo, 5% Fe, 4% W, 2.5% Co, 0.35% V, 1% Mn, 0.08% Si, and 0.01% C) used as the substrate. Hastelloy C 276 has high tensile strength and flexibility with a melting temperature of around 1350 °C. The roughness of Hastelloy surface is about 1 nm after electropolishing.
- 2) An amorphous Al_2O_3 layer (about 80 nm thick) is deposited by sputtering and this layer serves as a diffusion barrier. There is a possibility that some of the elements in the Hastelloy could potentially diffuse into the superconducting layer, due to the high processing temperature during the deposition of the various layers. The alumina layer has been found to be effective in blocking this diffusion.
- 3) An amorphous Y_2O_3 layer (7 nm thick) is deposited by sputtering. This thin layer serves as a seed layer for deposition of the next layer.
- 4) MgO layer (10 nm thick) is deposited by IBAD. This layer provides a template with the biaxial texture and is critical for epitaxial superconducting thin film deposition.
- 5) Homo-epitaxial MgO layer (about 40 nm thick) is deposited by reactive magnetron sputtering, in order to further improve the texture.
- 6) LaMnO_3 (LMO) layer (about 50 nm thick) is deposited by reactive magnetron sputtering process to achieve a better lattice match with YBCO. MgO has cubic unit cell with the lattice parameter of $4.2\text{\AA}$, while LMO has an orthorhombic unit cell with the lattice parameters of $a = 5.537\text{\AA}$, $b = 5.747\text{\AA}$ and $c = 7.683\text{\AA}$ [94]. The [100] or [010] of the LMO lattice has a good match with the [110] of the YBCO lattice.
- 7) REBCO layer (about $1\text{ }\mu\text{m}$ thick) is deposited by MOCVD and is described in section 2.1.
- 8) Ag layer (about $2\text{ }\mu\text{m}$ thick) is deposited by sputtering. The silver layer is needed for electrical contact to the superconducting film. It serves to transfer the current from the

- 9) superconductor to the Cu stabilizer layer that provides an alternate current path in case of local hot spots due to defective regions in the superconducting film.
- 10) Cu layer (about 20 μm thick on each side) is deposited by electroplating method on top of the Ag layer and at the bottom of the Hastelloy tape and serves as a stabilizer layer and provides an alternate current path.

The buffer tapes used in this research work are biaxially-textured IBAD MgO templates with a LMO cap layer on a Hastelloy substrate, as described above. The buffer sample length used for deposition of REBCO is 28 cm which is cut from a spool of a long buffer tape. Multiple tapes are processed in one run, while varying the process conditions such as susceptor temperature, oxygen flow, precursor recipes etc. Whenever during the deposition process the process conditions are changed, it was always ensured that there was enough leader tape (unpolished Hastelloy tape) between adjacent samples. This ensures process homogenization and stabilization of reactor conditions by the time the sample approaches deposition zone on susceptor. The exact position of each sample in the long MOCVD run is monitored by measuring the time from the start of the run. A leader tape with a length of 50 cm is used between adjacent samples. Each sample buffer is spot welded to a leader tape. Once all the buffer samples are welded, the prepared buffer sample spool is cleaned with a wet wipe containing methanol and the prepared spool is loaded into the MOCVD reactor.

2.2. Post MOCVD Processing – Silver Sputtering

Once the deposited REBCO samples are taken out of the MOCVD reactor, they are marked and cut into different pieces for electromagnetic measurements and materials characterization. The entire tape is silver sputter deposited using a R2R Silver Sputter tool. The silver cap layer provides a means of excellent solderability and good electrical contact. A DC magnetron sputtering system was used for silver deposition (Figure 2.5). The silver sputtering chamber is pumped down to a pressure of 8×10^{-6} Torr and then argon gas is used

to generate plasma at a chamber pressure of 3×10^{-2} Torr and a power output around 480 Watts. The thickness of the deposited silver layer is about $2 \mu\text{m}$ and is determined by the speed of the motion of the tape through the deposition chamber.

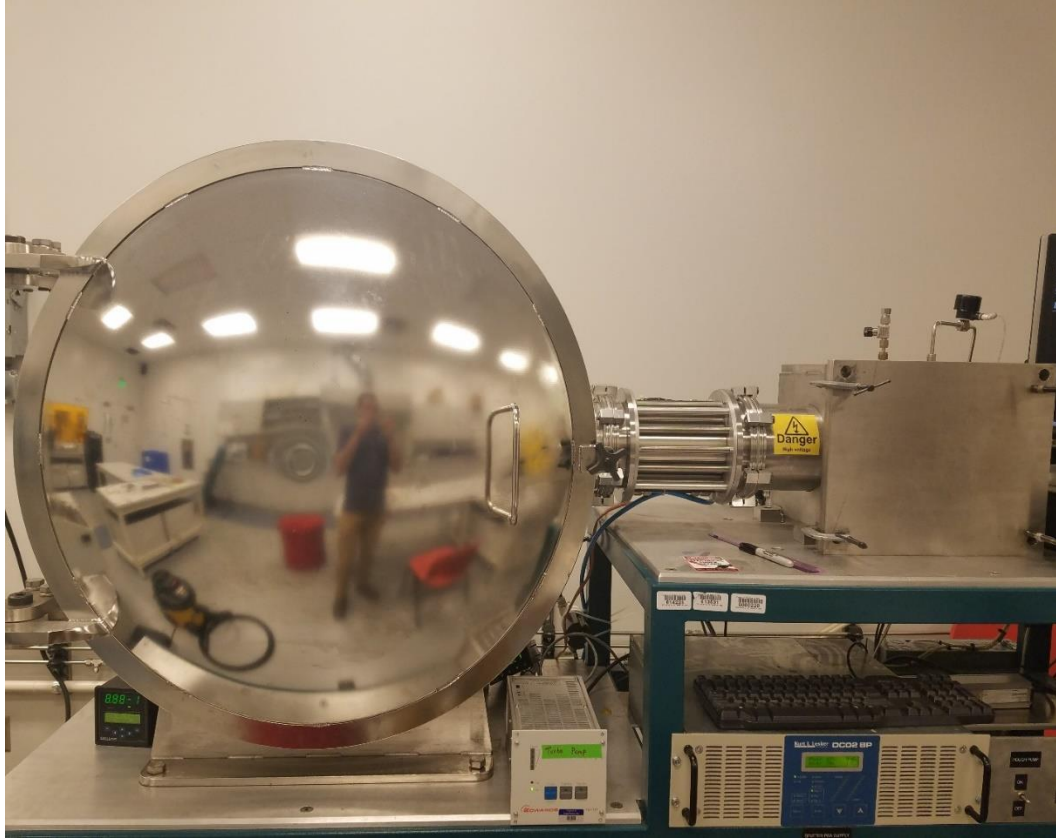


Figure 2.5 A DC magnetron R2R sputtering system used to deposit silver layer on top of REBCO films.

2.3. Post MOCVD Processing – Oxygenation

An oxygenation heat treatment is conducted to replenish the oxygen in REBCO film which enables transition from the tetragonal into orthorhombic structural phase. The REBCO coated conductors were placed in a horizontal tube furnace (Figure 2.6) and were oxygenated for half an hour at 500°C in oxygen flowing around 100 sccm, using temperature ramp-up and ramp-down rates of 180°C/h and 150°C/h respectively. After the samples were cooled to room temperatures, they were taken out of the tube furnace and sent for measurements and characterization.



Figure 2.6 Horizontal tube furnace used for oxygenation of REBCO thin films

2.4. Electromagnetic Characterization techniques for REBCO thin films

Several techniques were used for electromagnetic characterization of REBCO coated conductors. The main techniques used in this study are inductive I_c measurements using Scanning Hall Probe Microscopy (SHPM) and transport critical current (I_c) measurements and Physical Property Measurement System (PPMS) measurements for in-field magnetic properties of the coated conductors.

2.4.1. Inductive I_c measurements using Scanning Hall Probe Measurements (SHPM)

The critical current (I_c) of REBCO coated conductors was measured using a custom, in house built SHPM system to check the uniformity of the I_c along the length of the superconductor tapes and to correlate it with data obtained from the inline 2D GADDS XRD measurement. These kinds of correlations could be used to evaluate the properties of the thin film produced in real time and potentially be used as feedback signal into the process to alter the processing conditions accordingly.

SHPM enables rapid inspection of the I_c of coated conductors by contactless inductive measurements. Figure 2.7 shows a picture of the SHPM system used in this study.

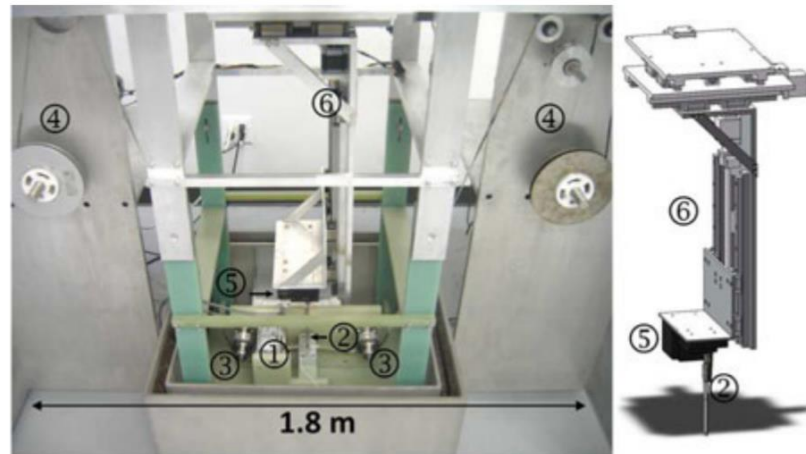


Figure 2.7 A photo of the SHPM system and a sketch of the Hall probe scan control system. 1) The magnetic loop, 2) Holder for the Hall probe, the probe is at the tip, 3) Roller cryogenic bearings, 4) Reel-to-reel tape motion system, 5) Fast scanning stage 6) 3D locating systems of the scanner. [87].

During the measurement, the tape is continuously driven by the reel-to-reel motion system from the left to the right. The tape is first cooled at zero field and then magnetized by the magnetic loop with a permanent magnet. The magnetic circuit is to focus the field and to greatly reduce the effect of reversing field at tape exit of the magnetizing zone. The peak flux

density in the magnetic loop is around 1 T, which is well above twice the penetration field of the samples, which ensures that the sample is in a critical state and the measured field profile yields the J_c . Due to thermally-activated flux creep, the trapped flux will decay with time. A typical time for the tape to move from the magnetization zone to the measurement spot is longer than 20 seconds. In the measurement zone, the Hall sensor is moving fast in the direction perpendicular to the tape motion in the tape plane, driven by the scanner as shown in Figure 2.7 as 5) and the position is recorded by an encoder. The whole fast scanning stage is fixed on a slow moving 3-axis motorized stage shown as 6), which allows horizontal positioning and height adjustment of the Hall sensor.

The effective area of the Hall sensor is $50 \times 50 \mu\text{m}^2$. The Hall sensor is excited by an AC current of 10~40 kHz, 10mA rms. The Hall voltage is analyzed by a Signal – Recovery 7265 lock in amplifier. The position of the Hall probe and the Hall voltage are collected by a high frequency data acquisition unit. The sampling rate is 10^5 Hz and the data is averaged afterwards by computer.

Figure 2.8 shows the SHPM measurement result on a 20 m coated conductor. For comparison, the measurement on a section of non-superconducting Hastelloy substrate tape at the end is also shown. The Fast Fourier Transformation (FFT) based method was used to calculate the current distribution in the tape as shown in Figure 2.7. The I_c of the starting section and the ending section of the tapes were also measured by four-probe transport method after the SHPM measurements. The FFT measurements were then scaled by a linear calibration factor to match with the transport measurements.

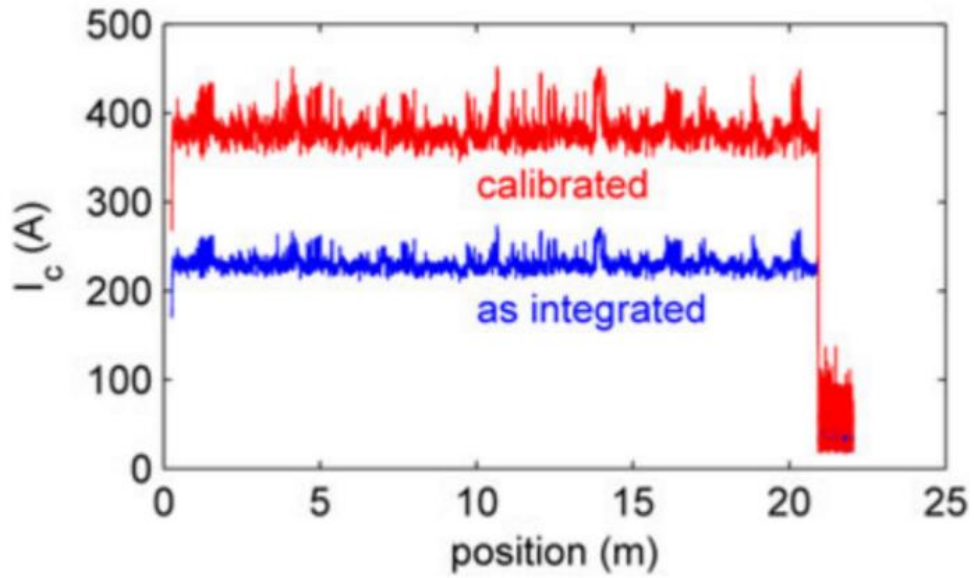


Figure 2.8 The calculated I_c from the SHPM data of the 20m CC. The blue line is direct integration of the FFT method calculated J_c , and the red line is after calibration using the four-probe transport measure of I_c of the starting and ending sections.

2.4.2. Transport Critical Current Measurements (I_c)

Transport self-field and in field critical current measurements were conducted on REBCO coated conductors using the standard four-probe method using a $1 \mu\text{V cm}^{-1}$ criterion. All the contacts in the four-probe method were made with indium solder which has a melting point of 160°C . The melting point of indium is low enough to protect samples from potential damage caused by heat. One of the biggest issue with the transport I_c measurements along the length (without making the bridge) is the sample burnout problem due to the high transport current passing thorough the superconductor. A significant joule heating is generated once the REBCO sample becomes resistive in a local region and could result in a drastic local temperature rise and cause a burnout damaging the sample permanently. A sample bridging method to proportionally reduce the transport current was developed, to overcome the sample

burnout problem and enable transport critical current measurements at low temperatures. The sample bridging method procedure is described as below:

- a) A bridge of approximately 1 mm in width and 10 mm in length is patterned on a silver sputtered REBCO sample with Kapton tape as a mask.
- b) The patterned sample is dipped into the silver etching solution which contains 50 vol% ammonium hydroxide (NH_4OH) and 50 vol% hydrogen peroxide (H_2O_2) solution until the exposed silver adjacent to the patterned bridge is etched away.
- c) Then the sample, after rinsing with tap water, is dipped into ten vol% nitric acid (HNO_3) solution for about 20 seconds to completely remove the REBCO layer adjacent to the bridge.
- d) Finally, the sample is rinsed with methanol and the Kapton tape is peeled away carefully.

The final appearance of the sample with the bridge is shown in Figure 2.9. To measure the width of the bridge accurately, the samples are inspected under an optical microscope with a magnification of 1000x after critical current measurements are performed.

The I_c value of the 12 mm wide superconductor tapes can be calculated using

$$I_c = \frac{w_0}{w} I_c^b, \quad (2.1)$$

where w_0 and w are the width of a REBCO coated conductor (12 mm) and the bridge, respectively. I_c^b is the obtained critical current at the bridge.

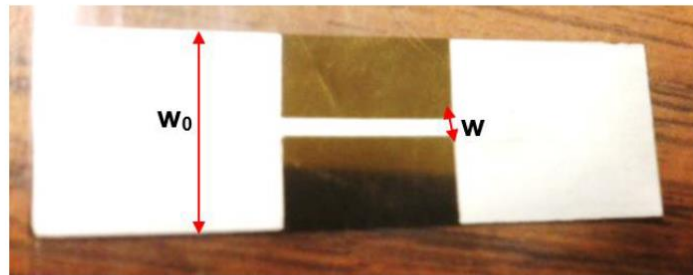


Figure 2.9 The REBCO sample with patterned bridge for transport I_c measurement.

Both the ends of the patterned REBCO sample are soldered to a pair of silver tapes obtained from Lucas – Milhaupt and the sample is attached to the sample holder assembly. The silver tapes are then connected to Cu cables which are attached to the electric current source. The entire assembly is dipped in liquid nitrogen during I_c measurement. A DC current provided by a power supply (Lambda, GEN – 3300W 600A) flows through the entire sample and the voltage on the sample is detected by two voltage tabs which are directly soldered on the REBCO coated conductor surface. The voltage is detected by a two channel nanovoltmeter (2182 A, Keithley). A schematic diagram is shown in Figure 2.10 with the position of the voltage and current tabs.

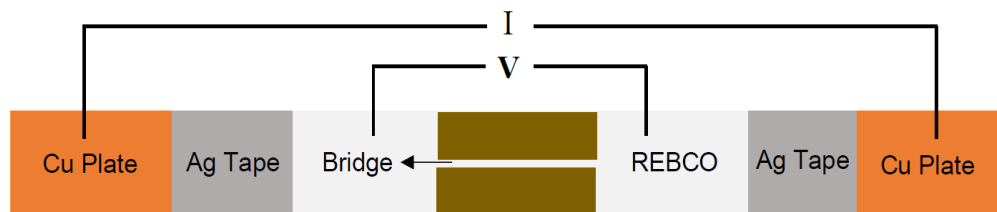


Figure 2.10 Schematic illustration of four probe method with positions of the voltage and current tabs.

2.4.3. Physical Property Measurement System (PPMS)

The Quantum Design PPMS Dynacool™ system was used for the measurements of a number of superconducting properties of the REBCO samples. Vibrating Sample Magnetometer (VSM) was used to measure the DC magnetization while the field was swept at a constant rate of 100 Oe s⁻¹. The magnetic J_c was determined from magnetization hysteresis loops calculated by the extended Bean's model as [95]

$$J_c = \left[\frac{20\Delta M}{a(1-(\frac{a}{3b}))} \right], \quad (2.2)$$

where a and b ($a < b$) are the width and length respectively of a rectangular cross section perpendicular to the magnetic field and the width of the magnetization hysteresis loop is ΔM (emu/cm³). Figure 2.11 shows a picture of the PPMS system used in this thesis for measurements.

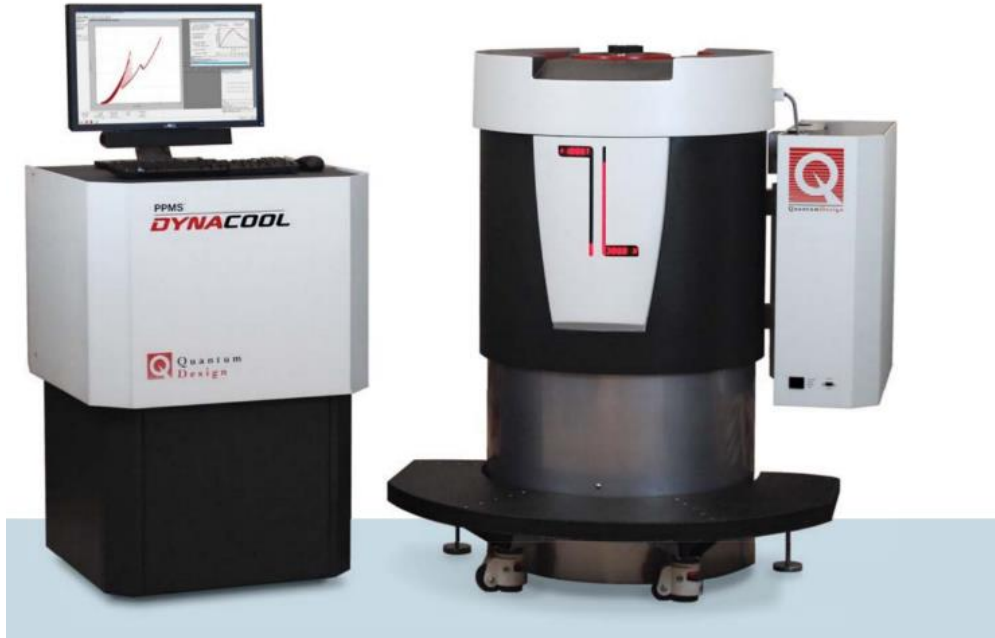


Figure 2.11 PPMS system used for studying the magnetic properties of superconducting samples.

2.5. Materials Characterization of REBCO Coated Conductors

Several techniques were used for materials characterization such as Inductively-Coupled Plasma – Mass Spectrometry (ICP – MS), General Area Detector Diffraction System (GADDS) XRD, Inline 1D and 2D GADDS XRD, and Scanning Electron Microscopy (SEM) which are described in this section.

2.5.1. Inductively-Coupled Plasma – Mass Spectrometry (ICP – MS)

The composition of REBCO films was examined by ICP – MS (Agilent Technologies 7700) with precisions at the level of a part of per billion (1 ppb). A detailed schematic of the ICP – MS set up used in this research work is shown in Figure 2.12. Multiple elements can be detected simultaneously with the ICP-MS to a high level of accuracy. Argon gas is used as a carrier gas for the solvent as well as the plasma gas for the Radio Frequency (RF) coil located inside the torch chamber.

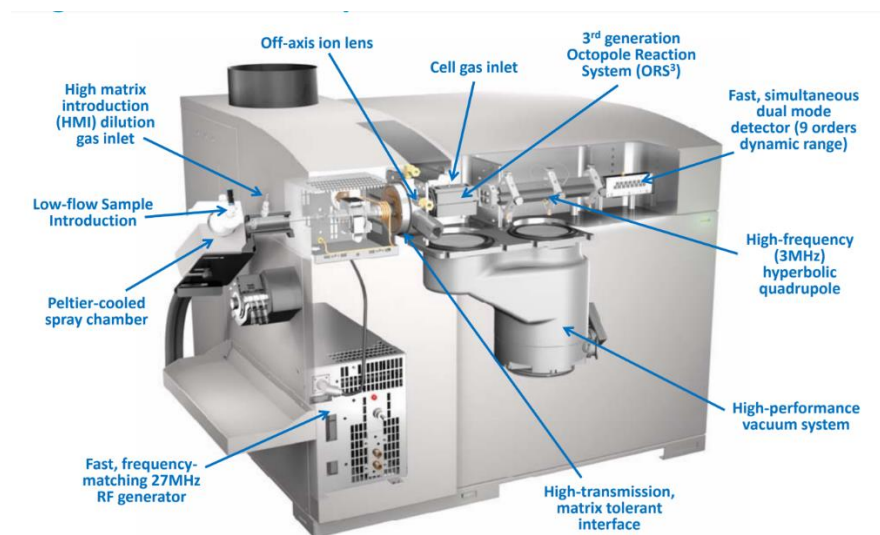


Figure 2.12 Schematic diagram of Agilent 7700 ICP MS system.

In this thesis, the REBCO samples (approximately 3 mm in width) were dissolved in 2 % Nitric acid solution (HNO_3) and the resulting solution was then introduced into the spray chamber via a nebulizer that forms an aerosol with a carrier gas of argon. These aerosol droplets were then passed through the plasma ($\sim 7,500\text{ K}$) provided by a RF coil inside the torch chamber. The plasma ionizes the elements in the solution by the removal of a single electron from the constituent elemental atoms in the aerosol solution. The beam of focused ions is next passed into the mass spectrometer via the sampling and skimmer cones and is narrowed down by the omega lens chamber. The quadrupole mass analyzer then filters the masses by allowing only one mass to charge ratio (m/z) of elemental ion to pass through it. The quadrupole mass filter consists of 4 rods (approximately 1 cm in diameter and 15 – 20 cm in length). They are further bifurcated into 2 pairs with opposing AC and DC electric fields applied to them respectively as shown in Figure 2.13. The resulting electric field is then tuned in such a way that only discrete values of m/z ratio passes through the system at one time; scanning across a span of voltage enables wide selection of elements to be assessed.

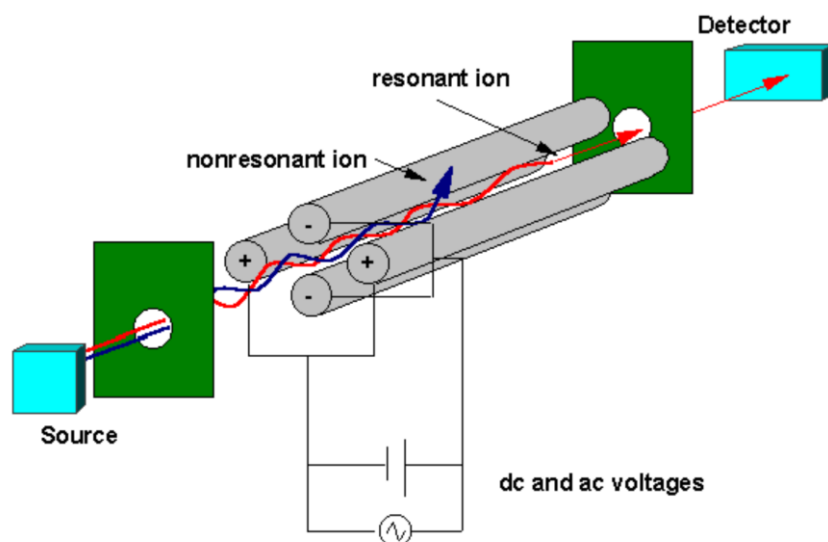


Figure 2.13 Schematic of a quadrupole filter.

An Octopole Reaction System (ORS) cell was also installed and studied in this thesis for improved signal resolution and removal of potential Polyatomic Interferences that might result at a given m/z ratio.

Further details pertaining to improvements made in the ICP measurements will be covered in Chapter 3.

The relative concentration of each element was obtained by dividing the measured concentration by its atomic weight. The normalized atomic percentage of individual elements was then calculated by dividing the relative concentration of individual elements to the sum of relative concentrations of all the elements.

2.5.2. 2-Dimensional – General Area Diffraction Detector System (2-D GADDS)

X ray diffraction data is obtained by using a Bruker AXS with Cu K_α radiation and a 2 D detector. GADDS is primarily used to investigate the crystalline characteristics of REBCO coated conductors on a 2D grid with more information obtained than a typical point detector. In these measurements (omega scan) the detector was fixed and the sample stage was moved continuously from 2° to 32° . The X-ray tube was operated at 40 kV and 40 mA and the X ray sources used in these measurements was Cu K_α ($\lambda = 1.5418 \text{ \AA}$) radiation.

2.5.3. In-line XRD – 1D and 2D configurations

A custom in-line XRD tool was used for characterizing the tapes in-line in a pilot-scale manufacturing tool. The in-line XRD system was initially setup with a 1D line detector capable of tracking both the REBCO (006) c-axis and the (200) a-axis peaks from the REBCO thin film. The XRD setup was operated in a symmetric theta – 2 theta configuration with omega ('alpha' axis in software) around 36 degrees and 2 theta ('Detector' axis in software) around 72 degrees. Since this machine uses a Cr K alpha source ($\lambda =$ This enables

us to capture both the (006) c axis REBCO peak and (200) a axis peak. The chi axis ('beta' in software) is usually kept at zero though there is also an option provided to oscillate the beta axis ± 0.5 degrees in order to capture the mosaicity of the REBCO grains of the tape.

The system was later upgraded from a 1D detector setup to 2D General Area Diffraction Detector system capable of tracking REBCO, barium zirconium oxide (BaZrO_3 - BZO) and rare-earth oxide peaks (RE_2O_3 - REO). In the 2D configuration, the omega axis is maintained at the lowest value of 12.5 degrees with the detector being maintained at around 23.5 degrees. Since the detector has a wide 2theta (~ 25 degrees) and chi span (180 degrees) in the 2D geometry, all the peaks from REBCO (003) to MgO (200) were detected along the [00L] zone axis. Off-axis peaks such as REBCO (103), BZO (101) etc. are also being captured at the same time enabling analysis of the physical structure of REBCO and secondary phases in real time. By being able to track several peaks of the primary and secondary phases simultaneously, a quantitative assessment of the tape can be made inline with potential correlations to in-field critical current which would be highly beneficial in ensuring uniformity of tape production in long lengths.

2.5.4. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) was used to investigate the variations in the composition of the precursor stream over time from the evaporator that is used for MOCVD deposition process. A novel sampling device with heated vapor lines was built in order to analyze the vapor gases formed inside the evaporator. A schematic of the setup is provided in Figure 2.14.

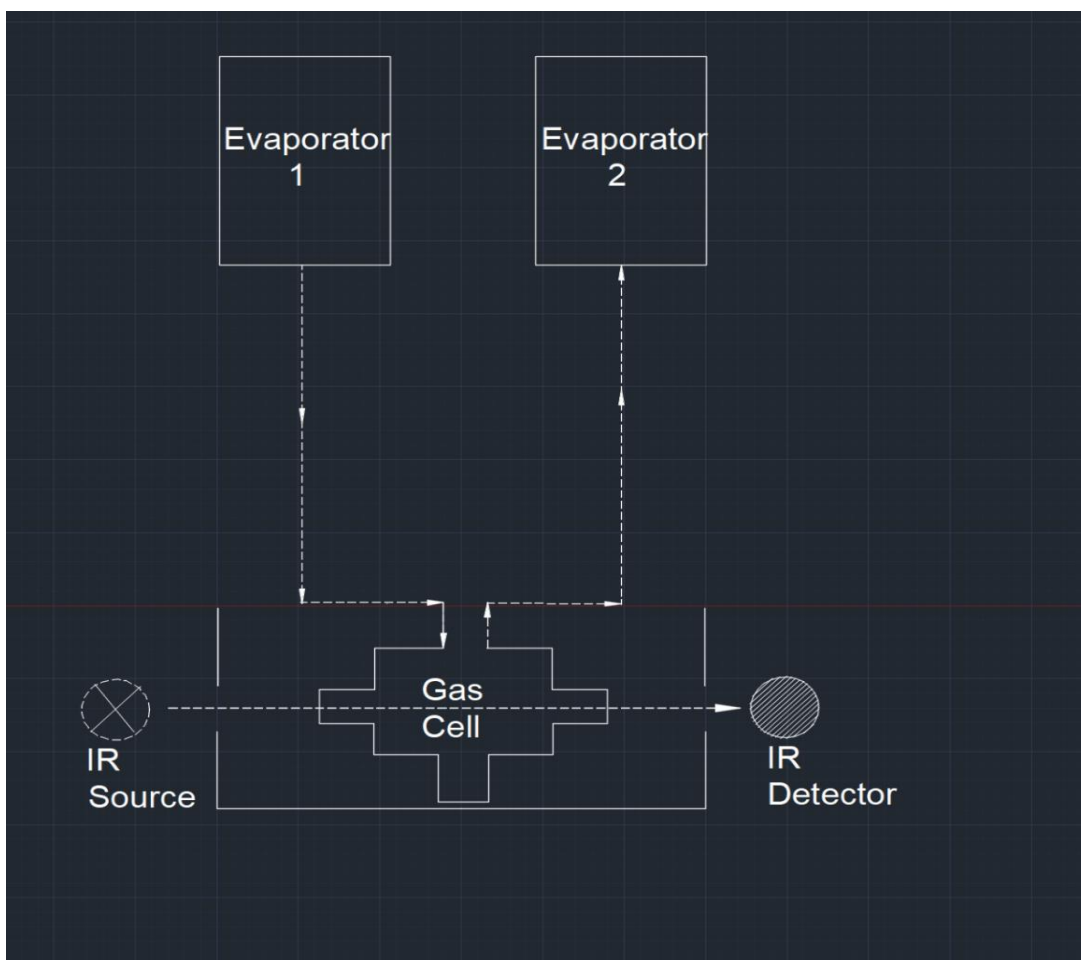


Figure 2.14 Schematic of FTIR experimental setup with MOCVD evaporators.

The precursors were fed into Evaporator 1 at precise feeding rates controlled by a metering pump and were vaporized under normal processing conditions. The vaporized precursor molecules were then drawn into a gas sampling device through heated vapor lines to avoid condensation. The sampling device was setup inside the FTIR machine between the infrared emitter and detector. The cell and the lines are heated up to 270 °C in order to prevent condensation of the precursor molecules in the vapor lines or the cell itself.

The gas cell is a fully enclosed vacuum chamber with custom KBr (potassium bromide) windows to detect signals with lower wavenumbers. The arrows in the diagrams on the vapor lines show the direction of vapor flow. The precursor molecules get pumped through the gas cell into evaporator 2 from whence they are diverted into the heated MOCVD

reactor. This will potentially prevent any gumming up of precursor residues in the main foreline and hamper the vacuum throughput of the system.

The fundamental operational principles behind FTIR gas analysis is relatively straightforward. Molecules in gas phase vibrate and rotate at frequencies characteristic to each molecule. Each frequency is associated with an energy state of the molecule. Infrared radiation (IR) moves the molecules to higher energy states and characteristic frequencies are absorbed by the molecules in the process. Each molecule absorbs infrared radiation at several characteristic frequencies or wavenumbers ($1/\text{wavelength}$; unit cm^{-1}). The result is an IR absorption or transmission spectrum which is a unique fingerprint of a molecule. The FTIR instrument itself in this study, is operated in transmission mode and the absorbed wavenumbers are plotted against Intensity.

Chapter 3

Inline X Ray Diffraction – 1D and 2D GADDs

3.1.1. Inline XRD – 1D setup

The Inline XRD tool was initially used in symmetrical theta – 2 theta mode in order to capture the peaks lying normal to the plane of the tape. Figure 3.1 is a schematic of this mode of measurement and Figure 3.2 shows a picture of the inline XRD setup with the different axes indicated for reference.

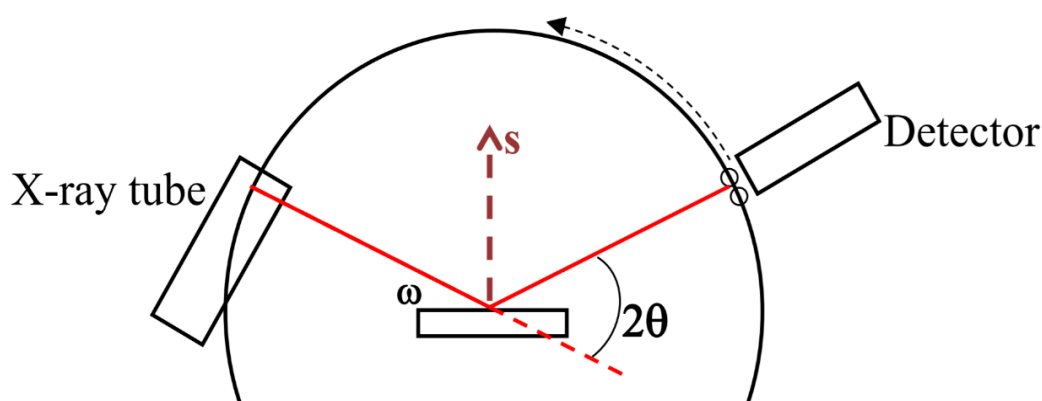


Figure 3.1 The incident angle ω is defined between the X ray source and the sample and is maintained at around 35 degrees. The diffracted angle, 2θ , is defined between the incident beam and the detector angle is kept around 70 degrees. Refinement around these values is performed before each measurement in order to ensure maximum peak intensity. s is the diffraction vector of the peak. [96].

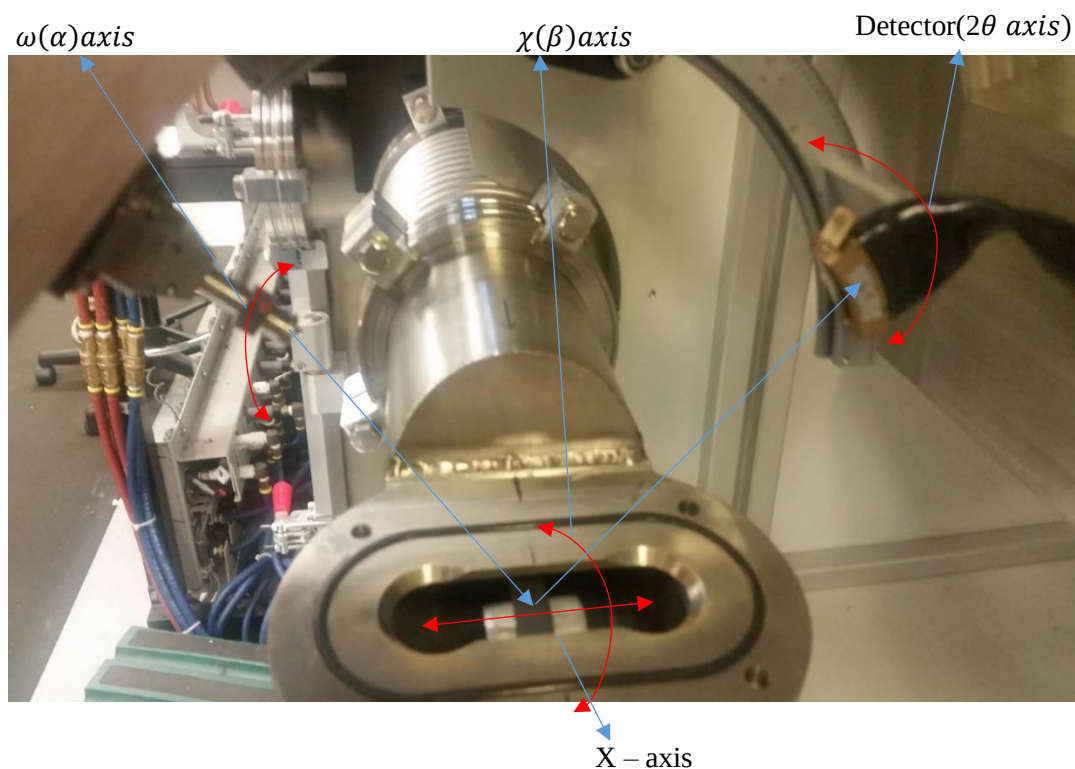


Figure 3.2 Picture of Inline XRD with the different axes labelled.

The tube axis is setup as the alpha axis, the chi axis as the beta axis and the 2-theta axis is setup as detector axis in the present software configuration. The chi axis alignment ensures capturing maximum peak intensity by accounting for the mosaicity of the tape along its length as explained in Figure 3.3.

The chi and x-axis also have the option of being oscillated between two fixed values during measurements and average out in order to capture variations along the length and width of the tape respectively. All of these measurements were done keeping the entire axis geometry static in order to reduce noise and smear induced due to motion of the setup to a minimum.

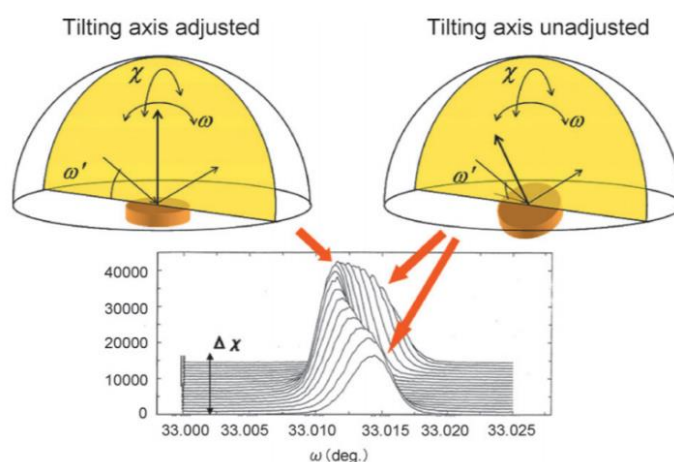


Figure 3.3 Effect on ω scan by misalignment of tilting axis.[97]

Initially the inline system was setup as an online quality-monitoring tool capable of tracking the output of the pilot scale production machine in real time and give feedback to the operators on the quality of the tape output. This information could potentially point to faults or errors in the production tool line and be used to change the processing conditions in order to improve the quality of tape. Figure 3.4 shows a single exposure obtained on a point on the REBCO tape. Both the (006) REBCO and (200) REBCO peaks are clearly visible.

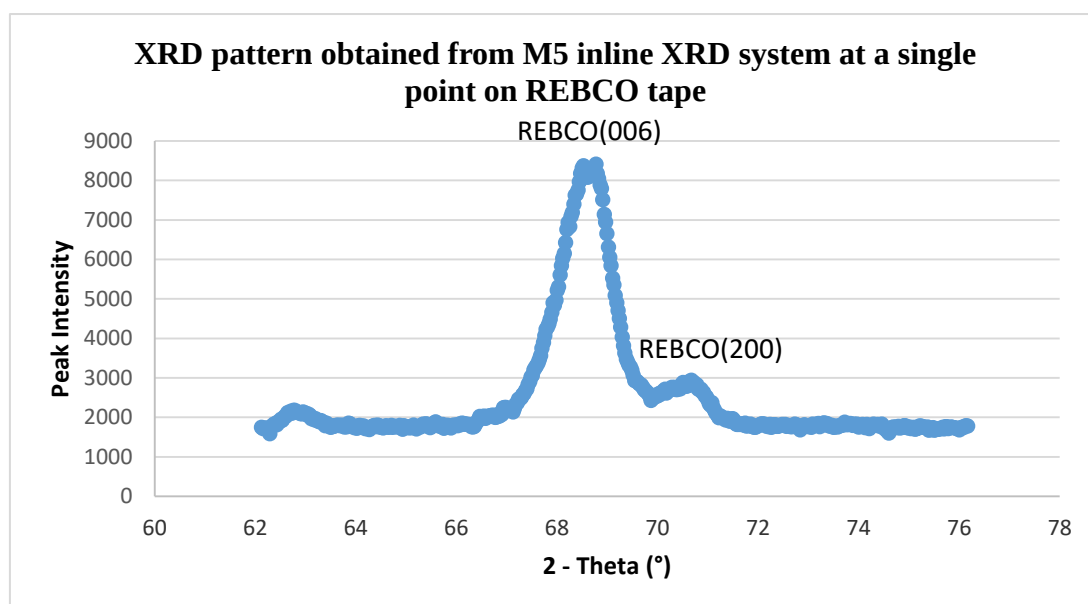


Figure 3.4 XRD pattern obtained from inline XRD system in pilot MOCVD tool on a spot on the REBCO tape.

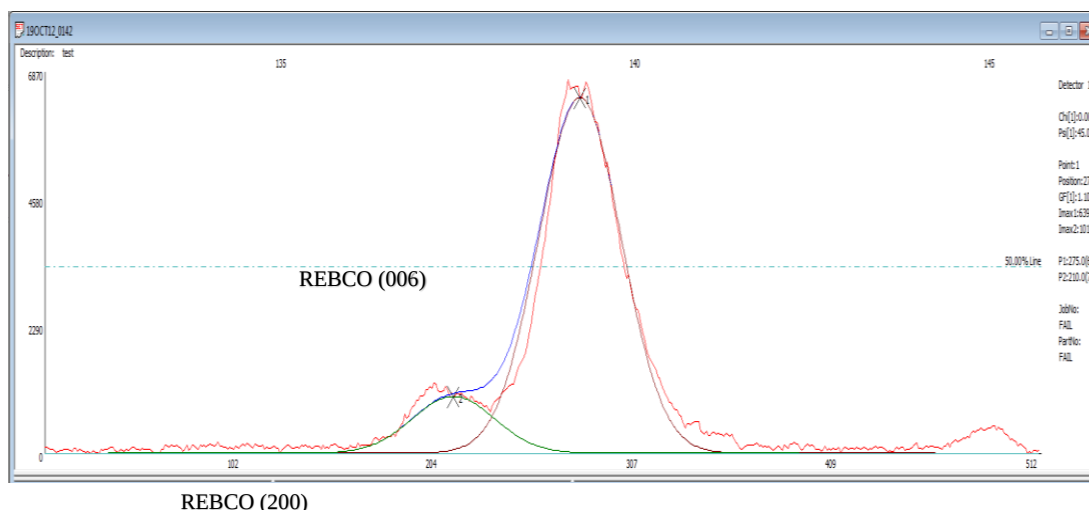


Figure 3.5 Screenshot of XRD software showing Gaussian peak fittings to capture both the REBCO (006) and REBCO (200) peaks.

Figure 3.5 is a screenshot of the software in action capturing both the peaks and fitting them to a Gaussian profile. The peak intensity, Full Width Half Max (FWHM), peak location etc. are captured in this fashion and recorded in a separate inline file which can be plotted in real time. Note that this image is flipped when compared to the previous image. This is because lower channel numbers are mapped to higher two theta values on the detector. Therefore, this image is flipped when plotting Intensity vs 2 theta.

Figure 3.6 is a plot showing maximum intensity of the (006) REBCO peaks captured along the length of a section of a REBCO tape. The tape speed was 6.6 m/hr and the acquisition time of each exposure was 7 seconds so the crystalline structural data is sampled at every 1.3 cm interval. The intensity of the peaks of the REBCO tape that is being measured exhibits significant non-uniformities potentially due to the poor thermal profile on the susceptor. This can be used as feedback information to the operator that the susceptor needs to be resurfaced i.e., sanding and polishing of the susceptor surface in order to yield a uniformly smooth surface that will ensure adequate physical contact with the tape for good thermal conduction.

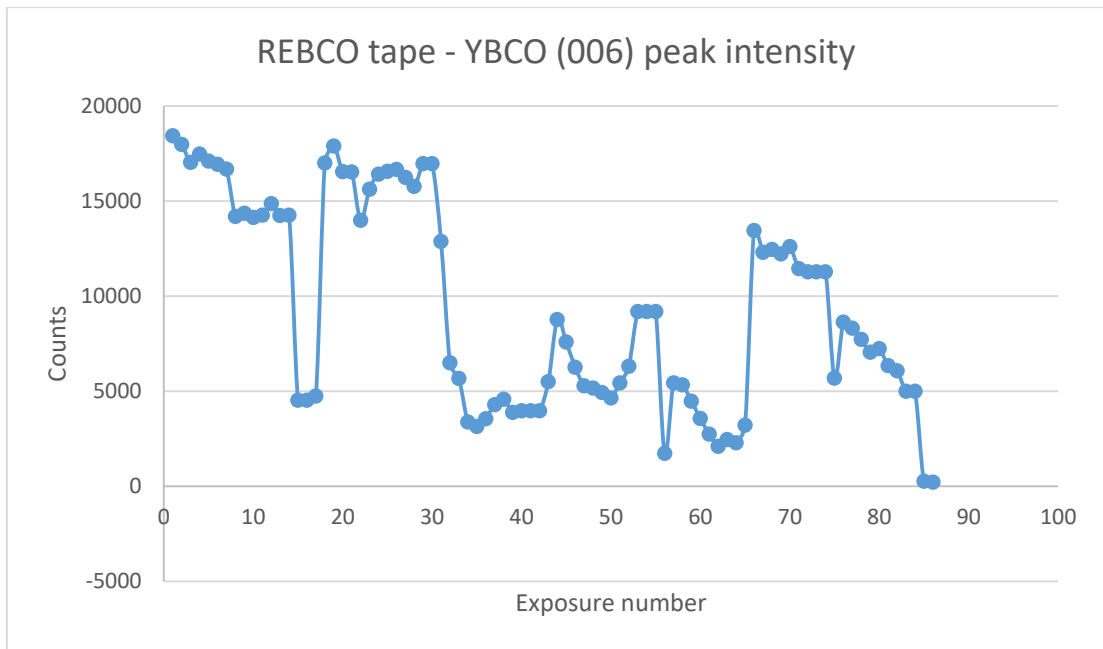


Figure 3.6 Peak Intensity REBCO (006) vs Exposure number on a section of a REBCO tape.

Figure 3.7 is a graph showing REBCO (200) peak intensity along the length of the tape. This graph captures important details about the regions where high concentration of a – axis REBCO grains can be found. These sections are not desirable and can later be correlated with processing/tool conditions in order to address the issues in future runs.

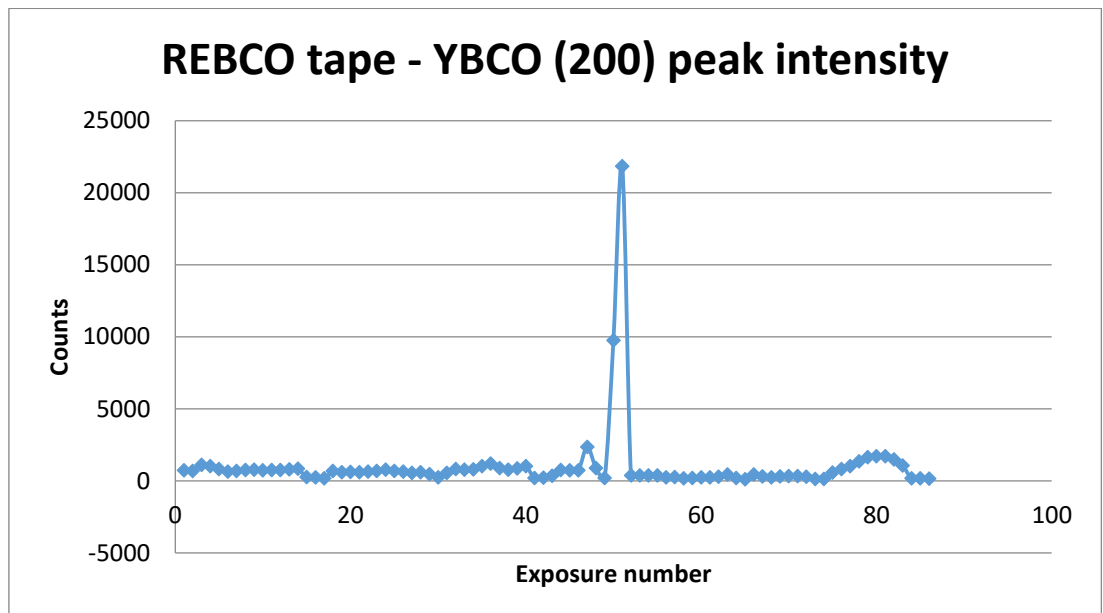


Figure 3.7 Peak Intensity REBCO (200) vs Exposure number on a section of a REBCO tape.

Figure 3.8 and Figure 3.9 are graphs showing the ratios of the peak intensities of REBCO (006) to REBCO (200) and REBCO (200) to REBCO (006) respectively. These

graphs can also be obtained as output from the software in real time and used to qualitatively evaluate the quality of the tape immediately. In Figure 3.8, the dips are regions of high a-axis grain concentration (or relatively smaller number of c-axis oriented grains) whereas in Figure 3.9, the spikes indicate regions of high a-axis grain concentration (or relatively smaller number of c-axis oriented grains).

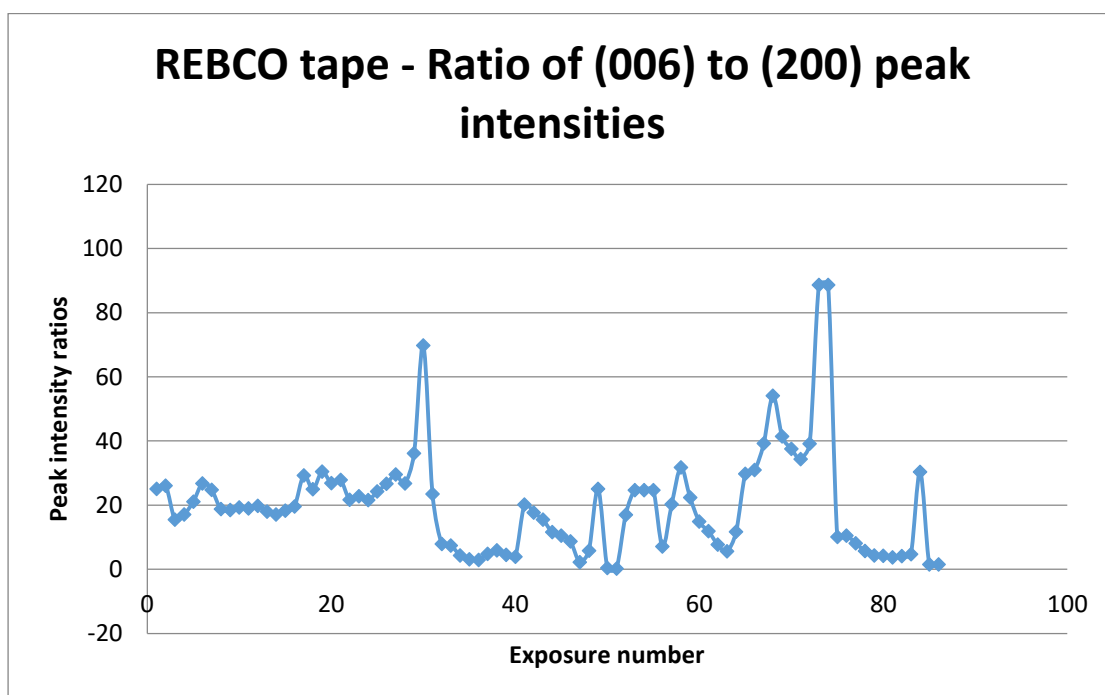


Figure 3.8 Ratio of REBCO (006) to REBCO (200) peak intensities.

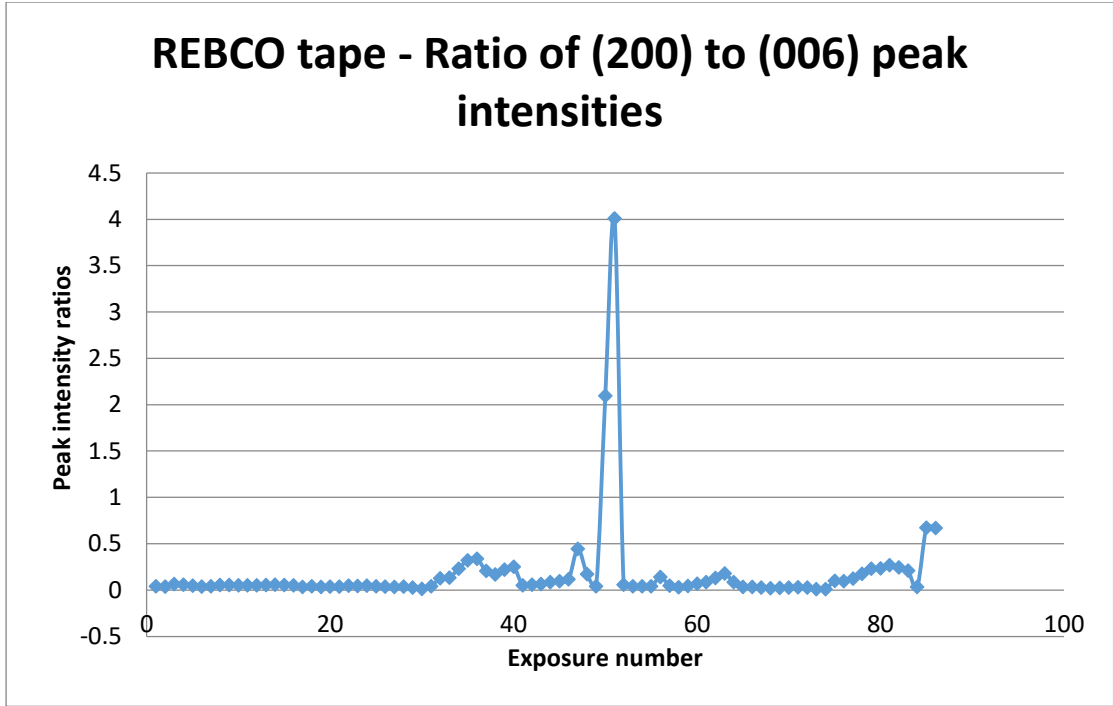


Figure 3.9 Ratio of REBCO (200) to REBCO (006) peak intensities

Incorporation of secondary phases such as BZO in the form of nanorods throughout the cross section of the tape can be approximated to a homogeneous strain acting on the REBCO crystallites in the c – axis direction. The amount to which the c – axis lattice parameter is strained would in turn be a function of the volume percentage of the incorporated BZO that is aligned along the c – axis direction of the REBCO crystallites (cation disorder due to barium substitution on the yttrium sites in the REBCO lattice also plays a role in this[85]). If we just assume one crystallite undergoing diffraction with the parameters d , λ , θ given by Bragg’s law, then the d spacings will be changed; a compressive stress would make the d spacings smaller and a tensile stress would make the d spacings larger. Then by Bragg’s law, the position of the peak will increase from 2θ to $2(\theta+\delta\theta)$ where

$$\lambda = 2d \sin\theta \text{ and} \quad (3.1)$$

$$\lambda = 2(d - \delta d) \sin(\theta + \delta\theta). \quad (3.2)$$

If every crystallite in the sample were strained (compressed) by the same amount, then they would result in a peak shift from 2θ to $2(+\delta\theta)$ as illustrated below in Figure 3.10.

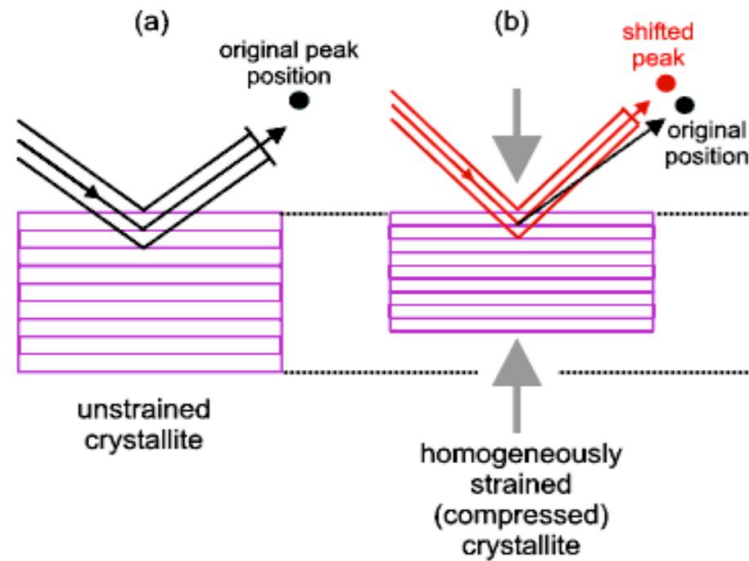


Figure 3.10 (a) Illustration of unstrained crystallite planes diffracting a peak under Bragg condition (b) Homogeneously-strained crystallite diffracting a peak with slight shift in position due to the influence of strain on interplanar spacing.

By using the inline XRD tool to monitor such subtle shifts in the 2-theta peak position, it is possible to evaluate the quality of the REBCO tape in real time. This tool would prove to be particularly useful when fabricating tapes of the same chemical composition and microstructure in longer lengths since any sudden changes in the lattice parameter of the tape can immediately be tracked and appropriate changes made to the processing conditions to bring the tape parameters back to nominal levels.

In order for this measurement to be successful, a fundamental issue regarding tape stabilization and variation of distance of the tape from the detector when the tape is in motion needs to be addressed. Bob He [98] gives the expression for diffraction space coordinates $(2\theta, \gamma)$ for a pixel at P (x,y) in a 2D GADDS detector setup as shown in Figure 3.11 as

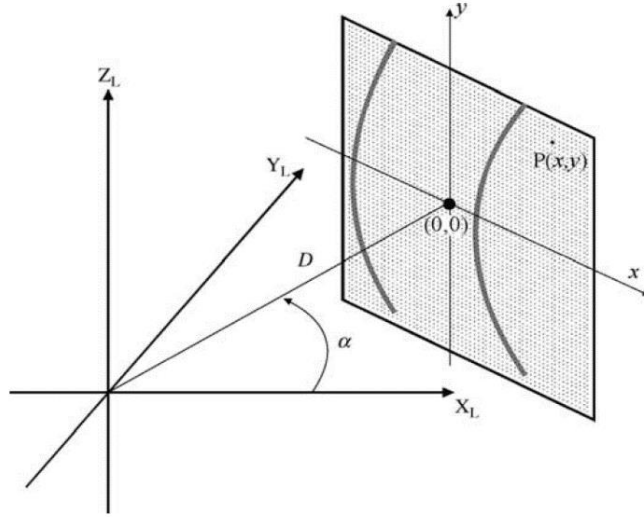


Figure 3.11 Relationship between a pixel P and detector position in lab coordinates, $X_L Y_L Z_L$

$$2\theta = \arccos \frac{xsina + D \cos \alpha}{\sqrt{D^2 + x^2 + y^2}} \text{ and} \quad (3.3)$$

$$\gamma = \frac{x \cos \alpha - D \sin \alpha}{|x \cos \alpha - D \sin \alpha|} \arccos \frac{-y}{\sqrt{y^2 + (x \cos \alpha - D \sin \alpha)^2}}. \quad (3.4)$$

The expression can easily be modified and calculated for a simple 1-D line detector with no γ or y -axis values. In order to confirm the effect of variation of sample-to-detector distance (D in equation 3.3), an experiment was conducted by varying the height of the goniometer setup with respect to the sample by varying the Z -axis position or the axis lying parallel to the normal of the tape. The tape is first brought into focus by using a touch pointer to make contact with the surface of the tape and fixing that point to be the focusing point as shown in Figure 3.12. The Z -axis is then moved in steps of 0.1 mm using an electronic encoder and the peak position variation is then tracked on the 1D detector.



Figure 3.12 Picture of inline XRD focusing arrangement. The setup has the option of moving along Z - axis in discrete steps of 0.1 mm.

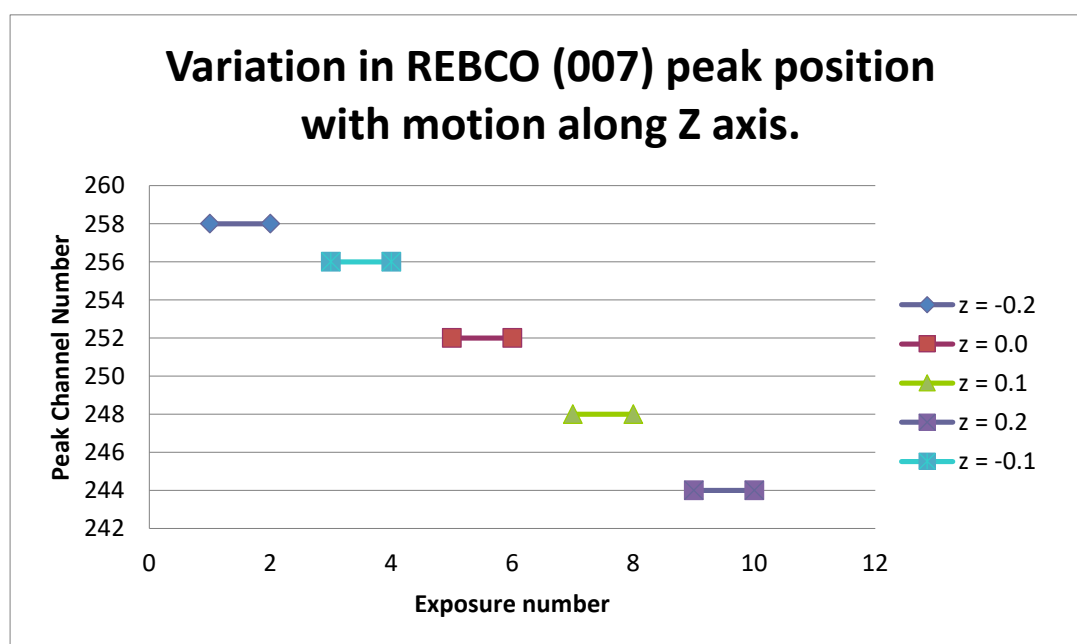


Figure 3.13 Graph showing the variation in the peak position of the REBCO (005) peak on the 1D detector upon moving 0.1 mm in the Z – axis direction. Z = 0.0 is the focused position of the XRD setup.

Figure 3.13 clearly illustrates the variation in the position of the REBCO (007) peak on the 1D detector upon varying the Z-axis height in discrete steps of 0.1 mm. Two exposures are taken at each height. Z = 0.0 is the focused peak position. Positive values of Z refers to

motion in the downward direction and negative values correspond to motion in the upward direction. The Peak Channel Number refers to the channel number on the 1D detector where the detector picks up the diffracted peak and has an angular range of 14.04 degrees split into 512 discrete channels. A variation of nearly four channels is observed upon varying the Z-axis height by just 0.1 mm. It can be clearly inferred from this graph that any measurement of real time variation in peak position is contingent upon maintaining a constant detector to sample distance in the XRD setup.

In order to make the tape motion mechanically smooth in the tape drive system of M5 and to maintain a constant detector to sample distance, a new smoothly-curved platform was designed and constructed capable of supporting the tape under tension and providing Z-axis stabilization during motion. Figure 3.14 is a CAD rendering of the new platform that was used for all the measurements. Fig 3.15 shows the platform as installed into the inline setup.

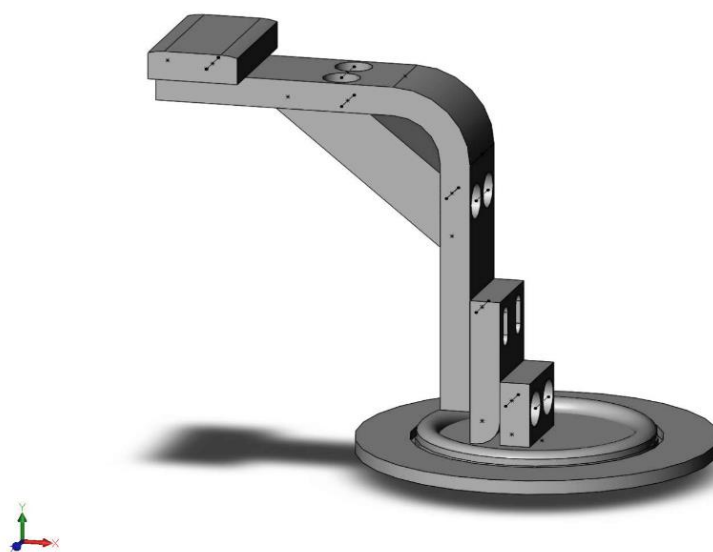


Figure 3.14 CAD drawing of the new platform



Figure 3.15 New platform as installed in the inline XRD system.

REBCO (007) peak was chosen for this study since it is a relatively isolated peak with no interference from secondary phases. The limit of resolution of the inline XRD system or the minimum change in the interplanar spacing that will result in a shift in the 2-theta value can be calculated using the following steps:

Bragg's Law is given as

$$\lambda = 2d \sin\theta. \quad (3.5)$$

Differentiating, the following expression is obtained

$$0 = 2d \cos\theta \delta\theta + 2 \sin\theta \delta d. \quad (3.6)$$

Rearranging the terms,

$$\frac{\delta d}{d} = -\cot\theta \delta\theta. \quad (3.7)$$

Substituting $d \sim 1.66 \text{ \AA}$ for REBCO (007) interplanar spacing, $\theta = 42.9^\circ$, and $\delta\theta = \frac{\delta(2\theta)}{2} = \frac{14.04}{(2 \times 512)} = 0.013^\circ$, in equation 3.7 it can be shown that,

$$\delta d = 0.01 \text{ \AA}.$$

Therefore, $0.01 \text{ \AA}$ is the minimum variation in interplanar spacing that will yield a systematic variation of 1 channel in the 1D detector. Note that this calculation will only hold for the assumption made in equation 3.6 that $\frac{\Delta\lambda}{\lambda} = 0$; in reality, even with the best monochromator, there is always a finite width to the K-alpha wavelength source, so the actual measured resolution will be much lower.

Six different tapes with a range of percentages of zirconium dopant were studied initially using the inline XRD setup. The atomic percentage composition of the six tapes obtained from ICP MS measurements are given below in Table 3.1.

Table 3.1 Compositions of tapes studied with inline XRD.

Sample ID	Cu	Y	Zr	Ba	Gd	(Ba + Cu)/Zr
M1 2714 1	48.7	9.2	1.9	31.7	8.5	0.69
M1 2714 2	45.8	9.2	3.2	32.8	8.8	0.79
M1 2714 3	46.4	9.4	3.1	32.3	8.9	0.76
M1 2714 4	45.4	9.6	3.1	33.1	8.9	0.80
M1 2714 5	45.3	9.5	3.1	33.2	8.9	0.80
M1 2714 12	44.3	9.6	2.4	34.8	9.0	0.84

The tapes were split into two batches for this study: 1, 2 and 12 were measured for the first batch and 3, 4 and 5 were measured as part of the second batch. The purpose was to examine the effect of lattice parameter variation with disparate and similar values of (Ba+Zr)/Cu ratios respectively.

For the first batch of tapes, HRXRD data were first obtained on all the tapes to compare with the data obtained using the inline XRD. Figure 3.16 shows the data obtained from the HRXRD for the first batch of tapes.

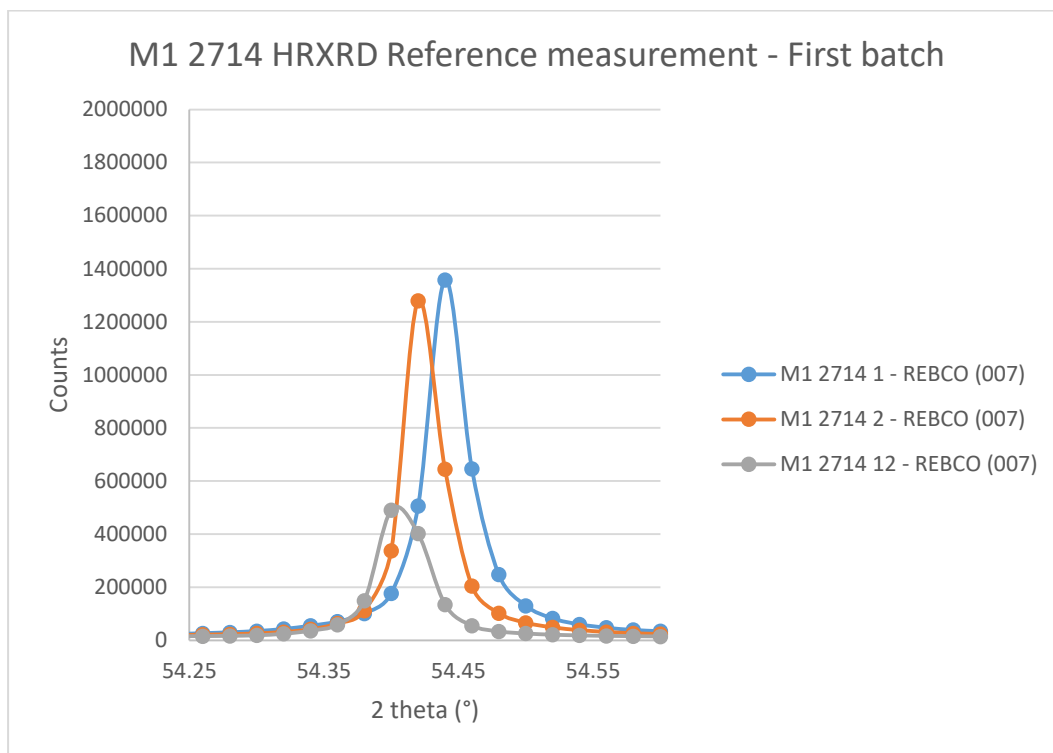


Figure 3.16 HRXRD data of REBCO (007) peak for first batch of samples.

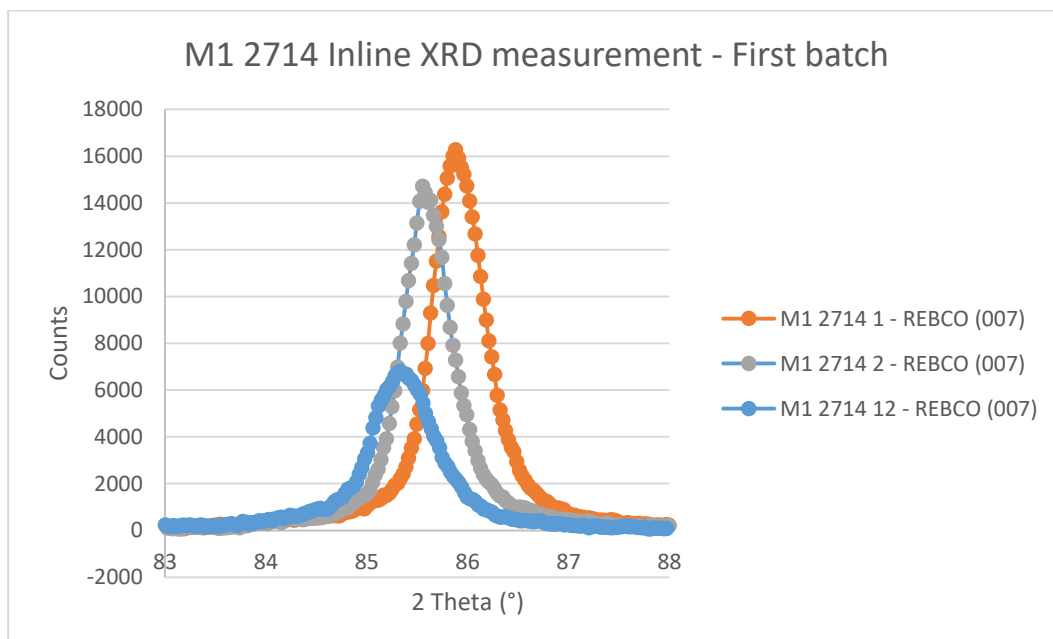


Figure 3.17 Inline XRD data of REBCO (007) peak for first batch of samples.

It can be clearly seen from comparing Figure 3.16 and Figure 3.17 that similar shifts in the REBCO peak positions occur in the XRD patterns obtained from both the instruments. The 2-theta positions of the peaks are obviously different in each case since the K-alpha wavelength of the X ray source being used is different. (Cu K alpha wavelength – 1.54Å vs Cr K alpha wavelength – 2.29Å). The ratio of the peak intensities for the different samples are also found to be slightly different but this can be accounted for the fact that a separate part of the sample was cut and measured in HRXRD and the rest of the sample was used for inline XRD measurement.

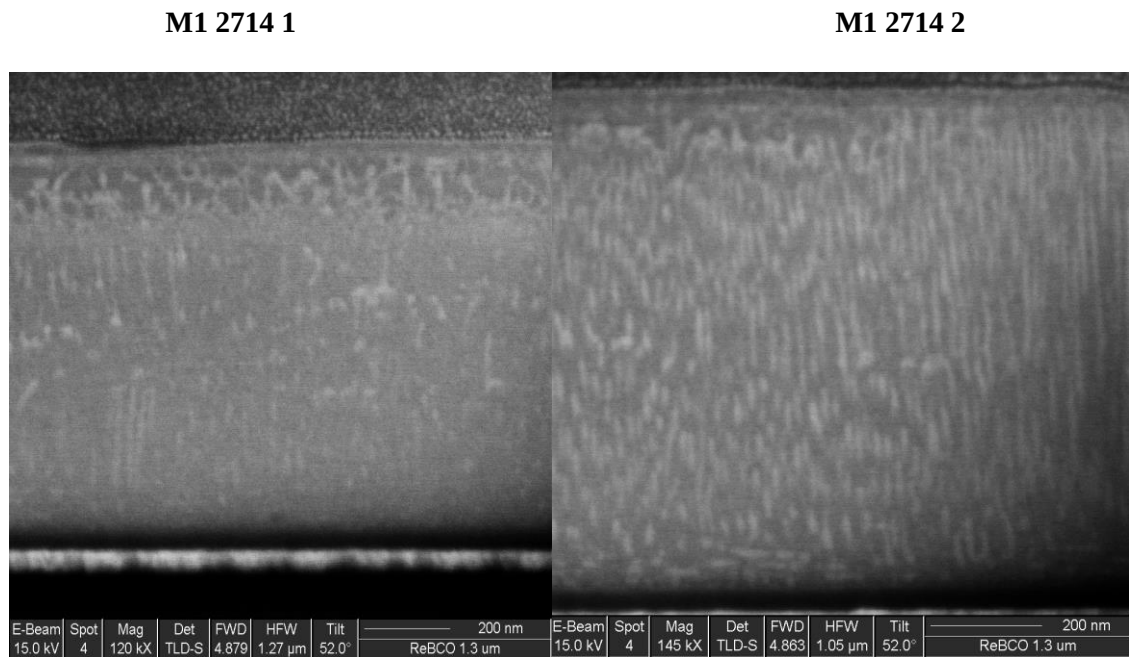


Figure 3.18 Cross sectional FIB images showing differences in BZO nanorod orientation and density between M1 2714 1 and M1 2714 2 samples.

It can be seen from Fig 3.18 that the density of BZO nanorods that are aligned in the direction perpendicular to plane of the tape along the c – axis of the REBCO film is far greater in sample M1 2714 2 than in sample M1 2714 1. Referring back to Figure 3.12(b), the inverse case of that diagram is at play here i.e., homogeneous strain acting along the c-axis direction in the tensile direction. This causes an increase in the lattice parameter of the REBCO lattice along the c-axis that can be tracked using the inline XRD as a decrease in the

2 theta value of the REBCO (007) peak. In this manner, by monitoring the peak position in the XRD setup, it is possible to ensure that the secondary phases are being engineered with the proper nanorod alignment in the preferential direction, all the other factors being kept constant. This approach will be used in tracking tapes of long lengths with the same chemical composition and microstructure since it can immediately point to any anomalies in the lattice parameters, which would indicate a shift away from desirable processing conditions.

The aforementioned data were obtained at a single point on each tape. The next step was to obtain data from a number of points across the length of samples and compare them to see if the instrument is capable of tracking and discerning between different tapes with good signal to noise ratio.

Figure 3.19 is a graph showing the variation in the peak channel number (position of the REBCO (007) peak on the detector) plotted against exposure number. Since the samples were short (5 – 10 cm in length), it was decided to perform one exposure per point and then move the tape around 0.5 cm before the next exposure. This would enable gathering of continuous data across the length of the tape since moving the tapes at even the slowest speed setting in the pilot MOCVD tape drive system (5 cm/min) would mean that only one or two data points would be detected on each sample with an acquisition time of 30 seconds per exposure.

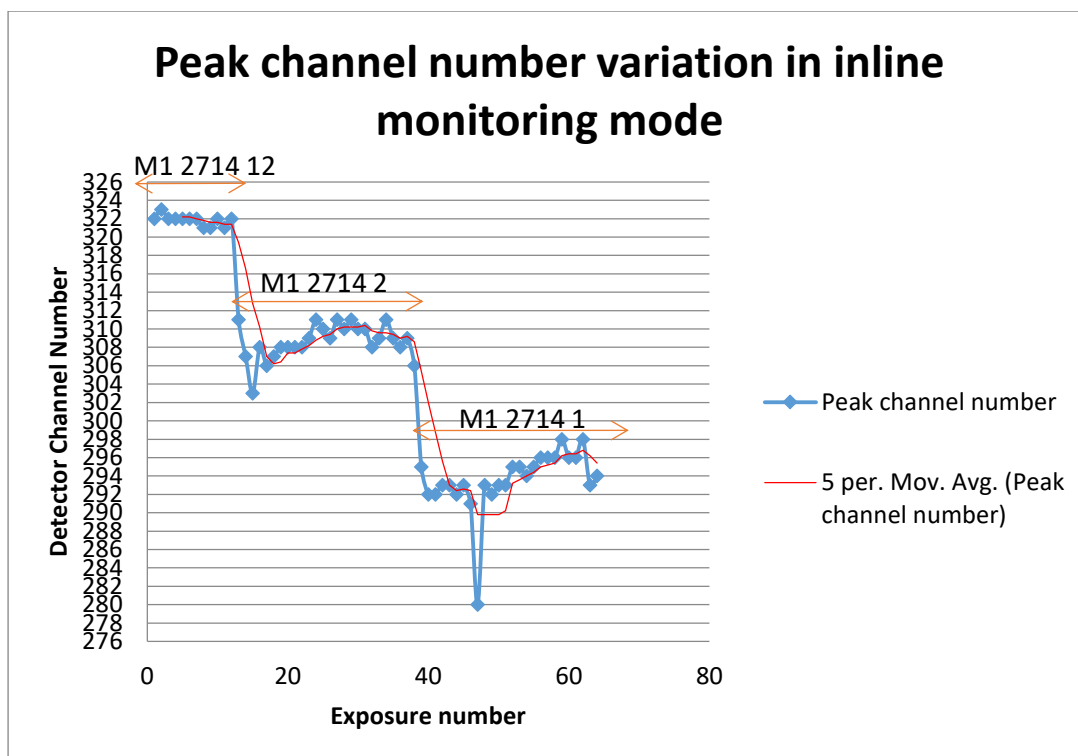


Figure 3.19 Peak position channel location on 1D detector vs exposure number. Higher peak channel number is mapped on to lower 2 theta value. A moving average with an interval of 5 readings is fitted as a smoothing function.

From Figure 3.19 we can clearly infer that the peak position of the REBCO (007) peak from the 1D detector is varying in a systematic fashion from one tape to the next. Higher channel numbers are assigned to lower 2-theta values and vice versa. A variation of 0.2 degrees corresponding to about 10 channels can be tracked accurately using this setup.

The second batch of tapes were measured next using the inline XRD system. This batch had two tapes M1 2714 4 and M1 2714 5 with the same values of (Ba+Cu)/Zr which

proved difficult for the system to discern. Figure 3.20 shows the REBCO (007) peaks obtained from one point on each of the three samples.

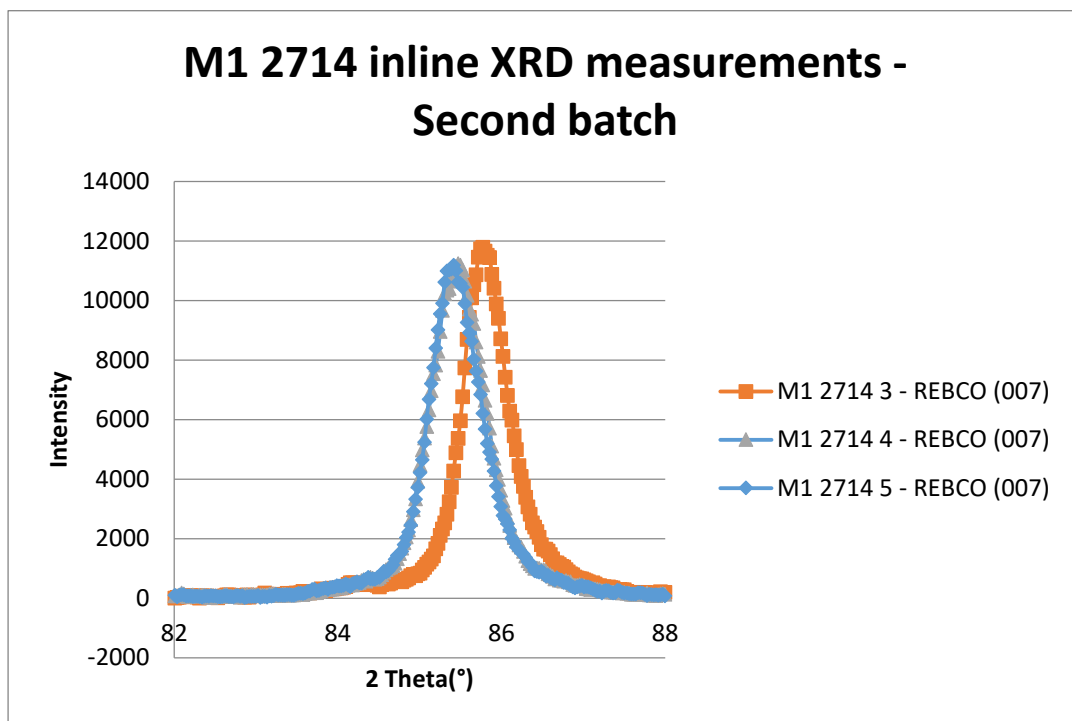


Figure 3.20 Inline XRD data of REBCO (007) peak for second batch of samples.

The same procedure as mentioned before is used to map out the variation in the lattice parameter across the entire length of the different samples as shown in Figure 3.21.

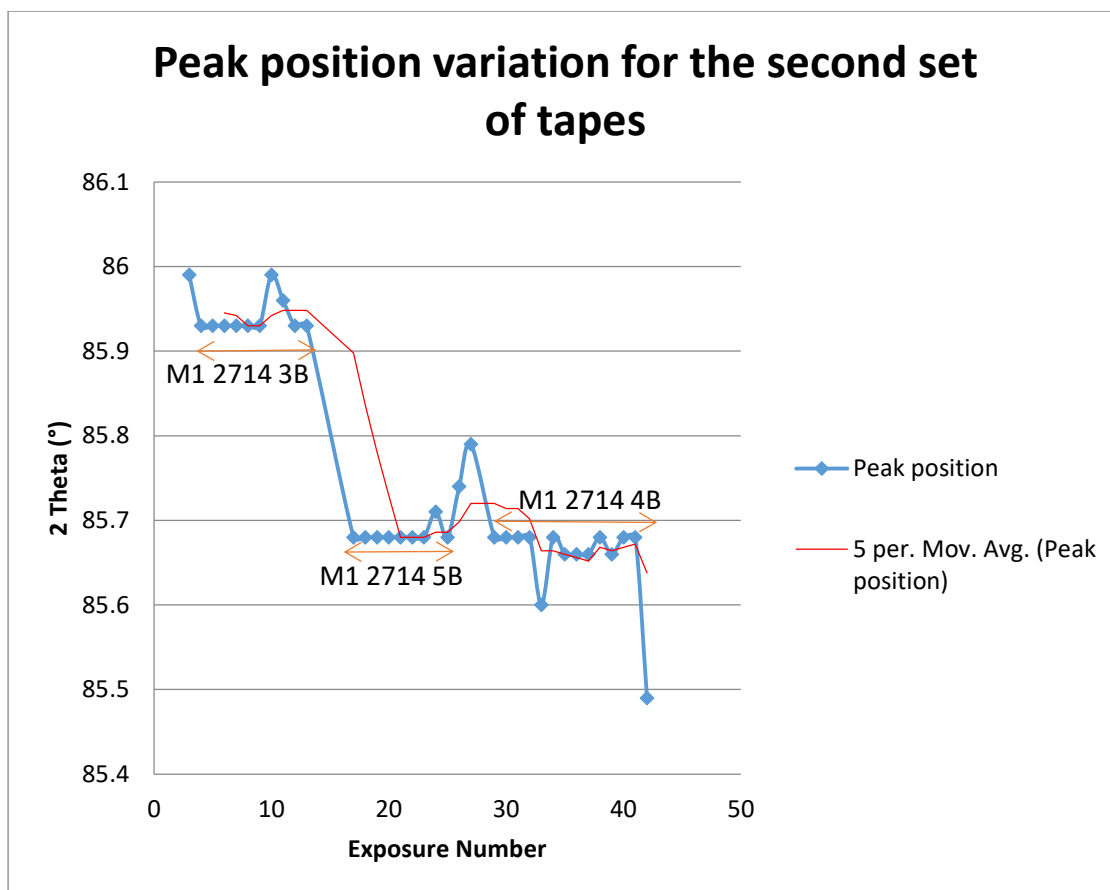


Figure 3.21 Peak position channel location from 1D detector vs exposure number. A moving average with an interval of 5 readings is fitted as a smoothing function.

It can be seen from Figure 3.21 that there is ample difference in the 2 theta peak position between sample M1 2714 3 and M1 2714 4 but M1 2714 4 and M1 2714 5 lie very close to each other and it becomes much harder to discern any tangible difference between the two tapes. This is a serious limitation of this metrological technique where the lattice parameter is used to indirectly detect the presence of nanorods along the c axis. Such issues will be addressed in the next section when the system was upgraded to a Two Dimensional – General Area Diffraction Detector system (2D – GADDs) where the primary as well as secondary phases are tracked in real time with geometrical feature observations that are purely a function of the intrinsic properties of the material itself.

3.1.2. 2D GADDS - Inline XRD

The fundamental idea behind streaking in XRD pattern that was explained in Chapter 1 can be explained as follows. Figure 3.22 shows a diffracted beam (angle 2θ to the direct beam) which is broadened over an angular range $2\beta \approx 4\delta\theta$. This is expressed by extending the reciprocal lattice point into a node of finite length, which, as the crystal rotates, intersects the reflecting sphere over this angular range.

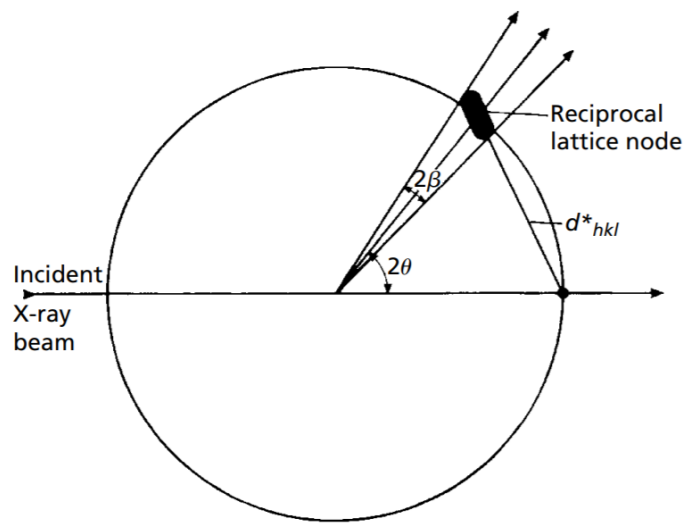


Figure 3.22 The Ewald reflecting sphere construction for a broadened reflected beam, β which corresponds to an extension $1/t$ of the reciprocal lattice node. [100]

Let $\delta(d_{hkl}^*)$ represent the extension of the reciprocal lattice point about its mean position. So,

$$|d_{hkl}^*| = d_{hkl}^* = 2 \frac{\sin\theta}{\lambda}. \quad (3.7)$$

A small change in d_{hkl}^* can be expressed mathematically as

$$\delta(d_{hkl}^*) = \delta\left(2 \frac{\sin\theta}{\lambda}\right) = 2 \frac{\cos\theta}{\lambda} \delta\theta. \quad (3.8)$$

Substituting for $\delta\theta$ from the Scherrer formula [100], $\beta = 2\delta\theta = \lambda/(t \cos\theta)$ gives

$$\delta(d_{hkl}^*) = 2 \frac{\cos\theta}{\lambda} * \frac{\lambda}{2t \cos\theta} = \frac{1}{t}. \quad (3.9)$$

i.e., the extension of the reciprocal lattice node is simply the reciprocal of the crystal dimension perpendicular to the reflecting planes, where t is thickness or dimension of the crystal perpendicular to the reflecting planes, d_{hkl} , of interest. This applied to all the other directions in a crystal with the result that the *shape* of the reciprocal lattice node is reciprocally related to the *shape* of the crystal. For example, in the case of thin, plate-like crystals (e.g., twins or stacking faults), the reciprocal lattice node is a rod or ‘streak’ perpendicular to the plane of the plate. This same phenomenon is observed in the 2D GADDS XRD pattern when the BZO phase is embedded in the form of fine nanorods along the c-axis direction of the primary REBCO phase and streaks perpendicular to the REBCO (00L) zone axis when the nanorod diameter is smaller. This smaller nanorod diameter, observed in the ab-plane view TEM micrographs, also contributes to the homogeneous strain in the REBCO lattice, which causes the peak position to shift as explained in the previous section.

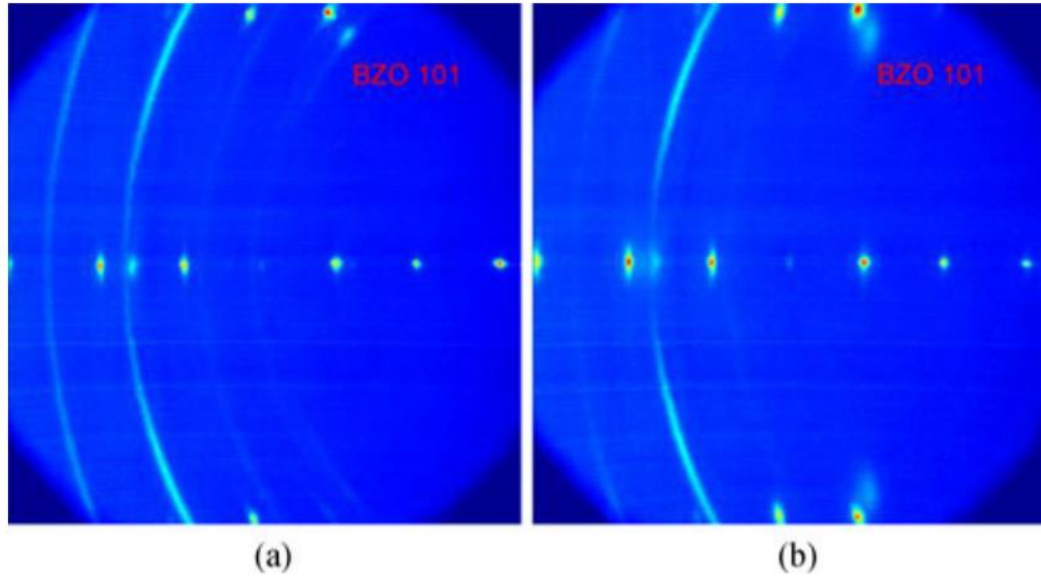


Figure 3.23. 2D-XRD diffraction pattern of two Zr-doped REBCO samples: (a) nanorod diameter ~ 20 nm and (b) nanorod diameter ~ 2 nm. Streaking of BZO (101) peak in the direction perpendicular to nanorod length is evident at small nanorod size. [84]

Figure 3.23 shows a pair of 2D GADDS scan of two samples with differing nanorod dimensions taken using an off-line XRD system. The BZO peak is well defined and if any streaking exists, it will be in a constant 2θ direction if the REBCO matrix also has sufficient out-of-plane texture spread, which the BZO will also follow. In contrast, if the nanorod diameter is small, there will only be a few scattering centers perpendicular to the nanorod length. This leads to the BZO (101) peak streaking perpendicular to the REBCO (00L) zone axis. If this information can be captured and processed in real time, samples with high lift factor which possess fine nanorods can readily be distinguished from samples with lower lift factor which are embedded with coarser diameter nanorods.

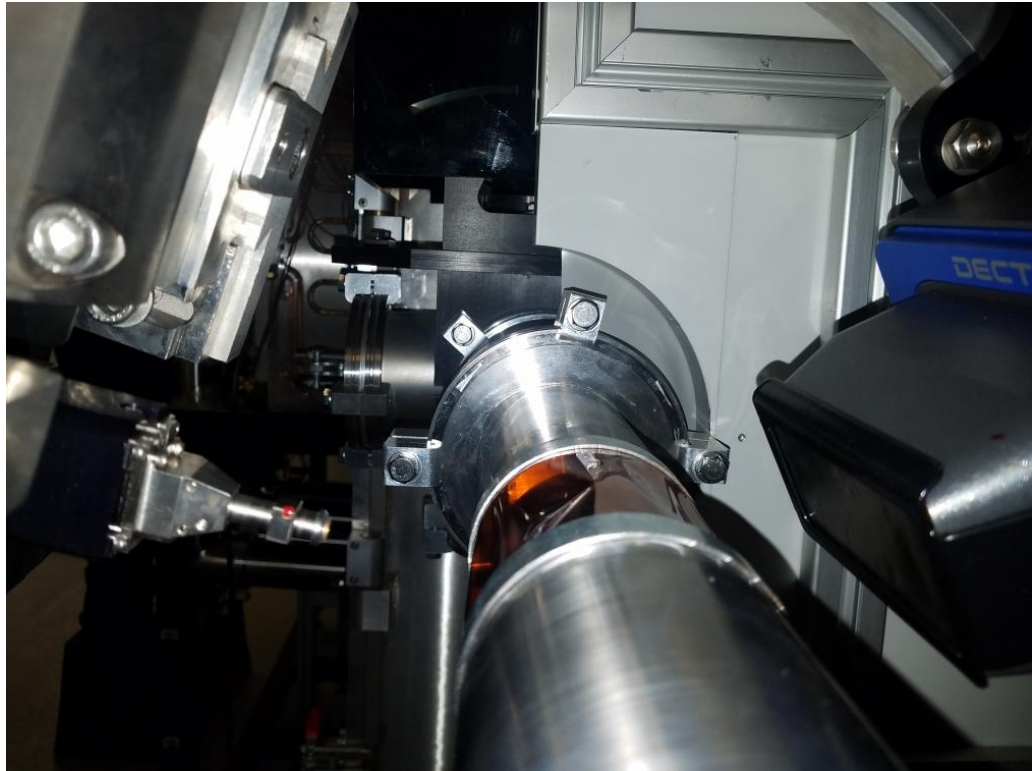


Figure 3.24 Photo of the new Inline 2D GADDS XRD system. The tape is brought into focus along the Z axis using the same touch point procedure as described earlier.

The software was custom designed to fit ellipses into the Regions of Interest (ROIs) by utilizing clustering based image thresholding based on Otsu's method [99]. As long as the zone axis [00L] lies perpendicular to the base of the XRD image, the tilt angle of the ellipses that are fitted to the peaks located at off-principal axis locations will track the peak streaking angle very closely. Figure 3.25 is an example of the XRD pattern with the peak fitting algorithm implemented to track REBCO (005), REBCO (103), and BZO (101) peaks. The (400) Re_2O_3 peak underneath the (005) REBCO peak is also clearly visible but not indexed in this particular image.

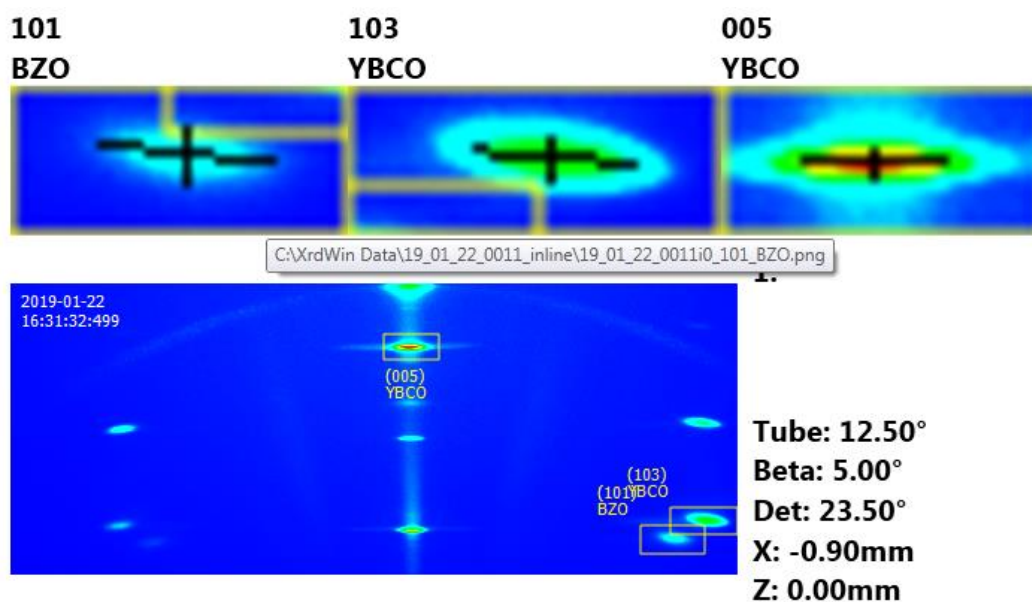


Figure 3.25 Sample XRD pattern showing different peaks obtained using inline 2D GADDS XRD pattern with three Regions of Interest (ROI) highlighted.

The tilt angle of the ellipse, which is the angle by which the semi-major axis of the ellipse deviates from a horizontal axis, is reported as the tilt angle of the peak which is the parameter of interest and is tracked in real time for inline monitoring. Figure 3.26 shows the geometric construction of the tilt angle.

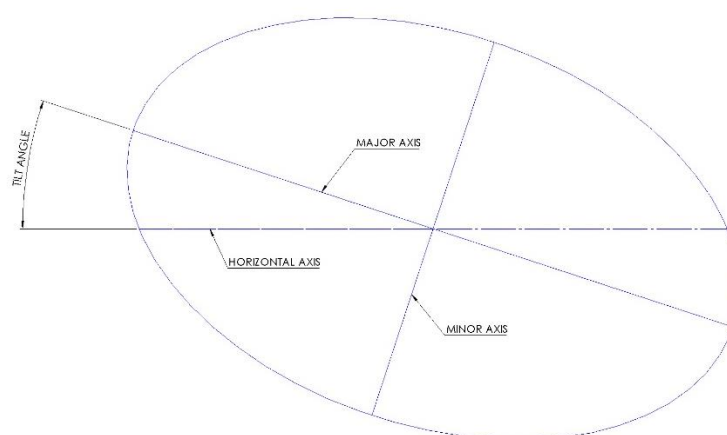


Figure 3.26 Ellipse showing the orientation or tilt angle ψ , which is a function of semi-major and semi-minor axis, a and b respectively.

It should be noted that the REBCO (005) peak with the [00L] principal axis is aligned perpendicular to the base of the image. Since the algorithm fits individual ellipses to separate ROIs, and calculates the tilt angle with respect to the base of the image, this is a necessary condition for accurate tracking of the tilt angle parameter. The geometric alignment of the Chi axis (β axis) in particular plays an important role in ensuring proper geometric alignment of the peaks. Several other parameters of the fitted peaks can also be tracked and plotted in real time. Table 3.2 shows the different parameters that can be captured and displayed in real time.

Table 3.2 Sample Output of 2D GADDS inline XRD measurements with all the fitted parameters.

Time	max_int	two_theta_breadth	unit_cell_a	unit_cell_c	major_a	minor_b	integrated_intensity	centroid	deg_tilt	chi_breadth	b_over_a	centroid_deg		
2019-04-01	3369	1.829845312	0	0	30.0825748	14.542274	803431	26.164111168	8.96869036	2.890264386	0.483395816	39.0247483178049	-36.2163614791809	
2019-04-01	3345	1.836062271	0	0	30.0979461	14.396984	798957	26.097099092	8.25214187	2.840796757	0.478337749	39.0233485548195	-36.2209484606537	
2019-04-01	3435	1.820988453	0	0	30.067651	14.442558	801080	26.141290507	8.54636684	2.889561315	0.480335443	39.0247026197202	-36.2218653746752	
2019-04-01	3373	1.846517361	0	0	29.9853627	14.530965	803881	26.086724278	8.07585275	2.882034629	0.484601951	39.017792290884	-36.2257588577867	
2019-04-01	3371	1.83999167	0	0	30.1499521	14.57676	808897	26.136620608	8.78030947	2.894952014	0.483475387	39.0201965031849	-36.2167254091902	
2019-04-01	3325	1.844578524	0	0	29.928724	14.547446	805521	26.080446071	8.88010035	2.894588552	0.486069691	39.01602950189	-36.2248540691392	
2019-04-01	3329	1.836903282	0	0	30.0659143	14.716745	814985	26.158108431	8.9926793	2.928659491	0.489482714	39.0181125484071	-36.2084733766674	
2019-04-01	3362	1.806934165	0	0	30.3345034	14.540457	813811	26.09095355	8.76385956	3.06989249	0.479337229	39.0162900687221	-36.2226079331153	
2019-04-01	3416	1.834562503	0	0	30.0164966	14.545269	812934	26.139616500	8.47574885	2.904011355	0.484575833	39.0202803818614	-36.2160985109523	
2019-04-01	3332	1.818879923	0	0	30.2899679	14.597705	817961	26.074828751	8.71757868	2.942272276	0.481932012	39.0134870475061	-36.2226948532758	
2019-04-01	2260	1.245035721	0	0	28.038072	11.648603	364243	24.690116212	27.0810535	3.197017591	0.415456618	38.8814283342313	-35.3845852748409	
2019-04-01	2269	1.244096646	0	0	27.5788357	11.541761	359669	24.762873642	25.9893671	3.293332905	0.418500659	38.8791006847084	-35.3630924585366	
2019-04-01	2220	1.252794898	0	0	27.9296598	11.58784	363649	24.694045631	26.1469603	3.291024698	0.414889369	38.8800387633222	-35.3816142800369	
2019-04-01	2214	1.274290694	0	0	27.8122148	11.485473	360718	24.660186073	25.9883104	3.186997035	0.412965076	38.878764144233	-35.3882391891063	
2019-04-01	2247	1.258146432	0	0	28.1302863	11.64032	369703	24.579530055	26.2019579	3.288296005	0.413800271	38.8635457162919	-35.3865739541436	
2019-04-01	2256	1.235459407	0	0	27.8766485	11.570625	366604	24.641419624	26.3733077	3.28188722	0.415065146	38.8658951671727	-35.3744864679635	
2019-04-01	2215	1.269834338	0	0	27.6845284	11.748045	369511	24.820059484	26.683245	3.245856076	0.424354168	38.8748624383323	-35.3427433023599	
2019-04-01	2251	1.254324334	0	0	28.2471992	11.762879	374618	24.540080825	26.1879336	3.299862786	0.416426381	38.8524802898588	-35.3805685454331	
2019-04-01	2241	1.240355527	0	0	27.6161518	11.677555	367344	24.617157215	25.8466682	3.216261982	0.422852366	38.8595514668515	-35.3714525737496	
2019-04-01	2245	1.281896159	0	0	27.3991278	11.674612	364312	24.615348931	26.4110099	3.185584261	0.426094291	38.8621001594258	-35.37555750885	

In order to check the calibration and uniformity of output of the instrument, the first sample to be tested was a piece of commercial reference tape with relatively uniform properties. This will act as a reference/control sample, manufactured by an industrially-proven process, for comparison with the other samples made with the newer AMOCVD process.

The algorithm exhibits some level of variation in the peak fitting parameters over time even if a number of exposures is collected repeatedly at a single point. So an experiment was conducted to study the variance in the value of tilt angle by collecting ten exposures at a single point repeatedly and incrementing the dwell time by 90 seconds after every 10 exposures.

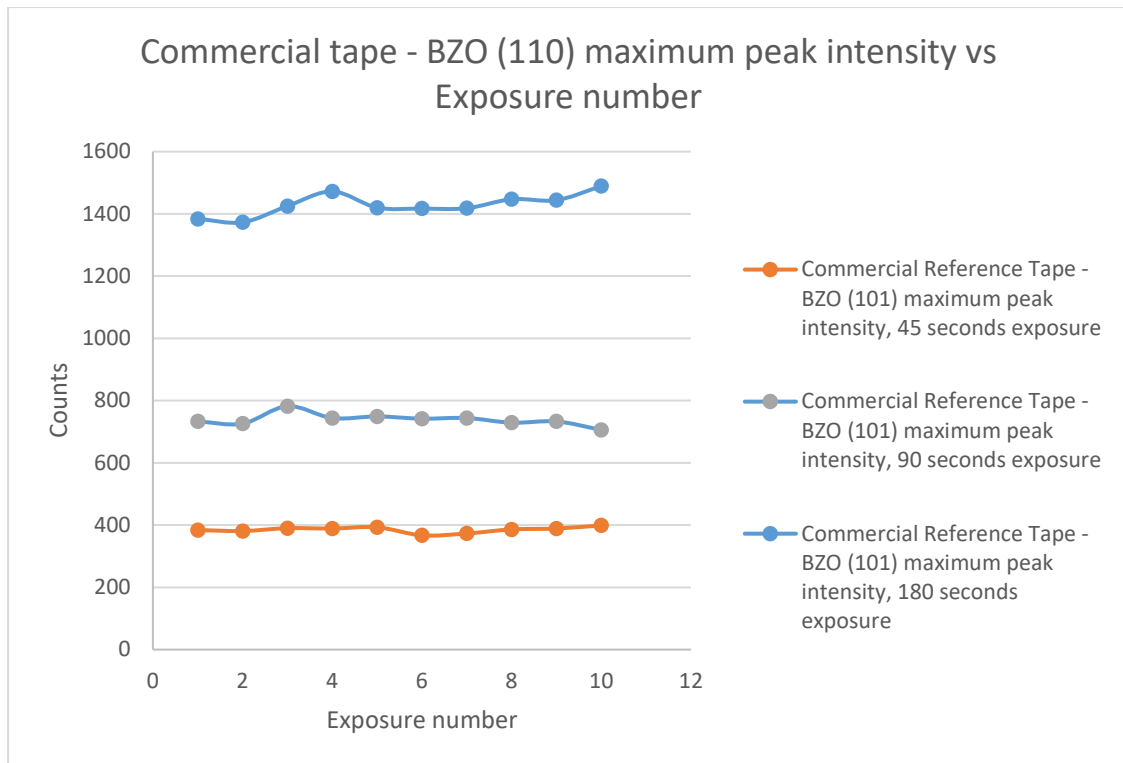


Figure 3.27 Variation in maximum peak intensity of BZO (101) on a single point on commercial REBCO tape with different dwell (exposure) times.

It can be clearly seen from Figure 3.27 that the peak intensity doubles with doubling the dwell time. Figure 3.28 shows the variation in the tilt angle of the elliptical fitting to the BZO (110) peak with increasing dwell time.

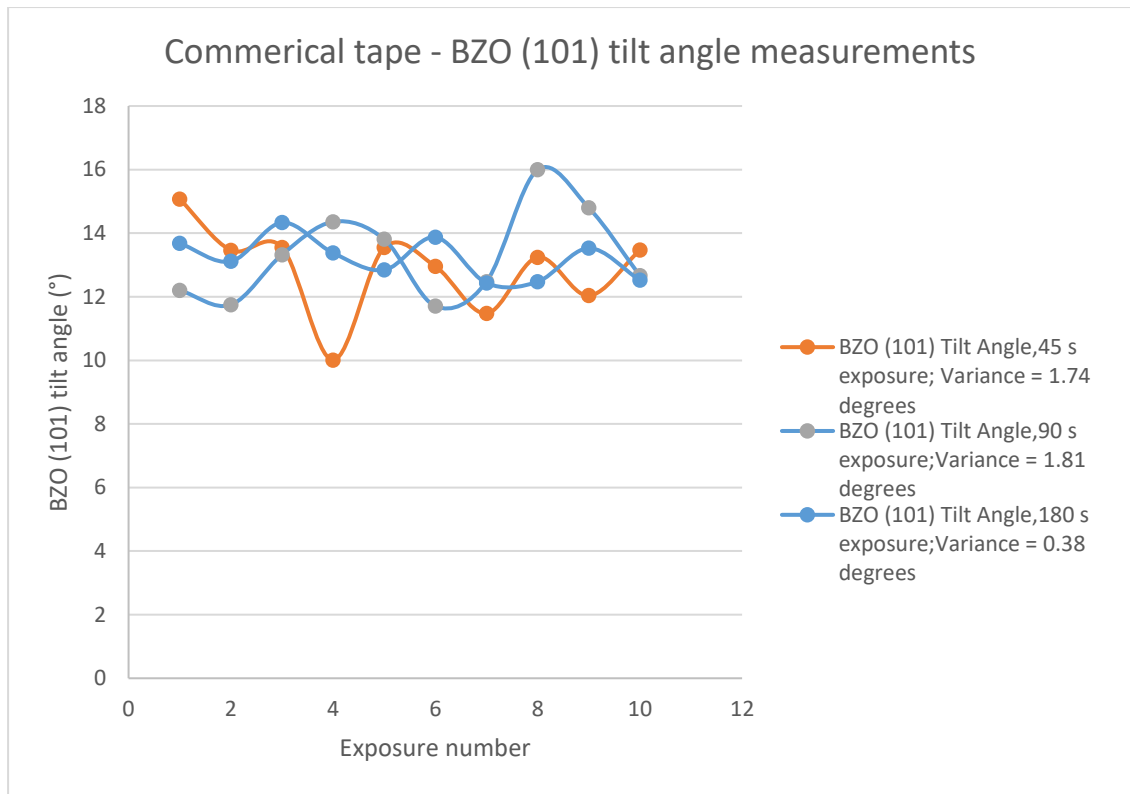


Figure 3.28 Variation in the tilt angle of the elliptical fitting to BZO (110) peak at a single point on commercial REBCO tape with exposure number.

However, it can be seen from Figure 3.28 that the variance in the set of ten exposures is not substantially affected in doubling the exposure time from 45 seconds to 90 seconds. It is in fact seen to increase slightly though this may be attributed to noise and is almost negligibly small (0.07° increase). Increasing the exposure time to 180 seconds substantially reduces the variance in the peak fitting by almost 80 percent but at the cost of a very slow sampling rate. Every point is averaged out over the distance travelled by the tape in 180 seconds. Dwell time is an important parameter in deciding the sampling rate of the measurement. Increasing dwell time leads to increased accuracy and resolution in being able to discern small variations in the tilt angle with reduced noise contribution from the algorithm but at the cost of very slow sampling rate with averaging over long distances. So any variations or trends that happen as a result of faster fluctuations in the processing parameters might not be detected although long term trends can be tracked given sufficient length of tape.

If the dwell time can be reduced to half with no major deterioration to the quality of the measurement (from 90 seconds to 45 seconds as shown in Figure 3.28), then more points can be sampled along the length of the tape, leading to a more robust and faster inline monitoring system that can track changes in the processing conditions more rapidly although the noise contribution from the algorithm increases substantially. So finer variations in the quality of the tape is traded off for faster response time. This is a tradeoff that has to be decided by the operator depending upon the observed time constants of the reactor and experience with the machine processing parameter variability over time.

In order to check the calibration of the instrument, a reference measurement was first obtained using commercially manufactured REBCO tape. Uniform characteristics are to be expected from such tapes and this will ensure the accuracy of the following measurements as well. The tape was measured at regular intervals of approximately 1 cm and ten exposures were collected at every single point with a 90 second dwell time and a 1 mm slit. These experimental conditions will be kept constant through the remainder of this thesis in order to keep consistency in the measurements for comparing samples.

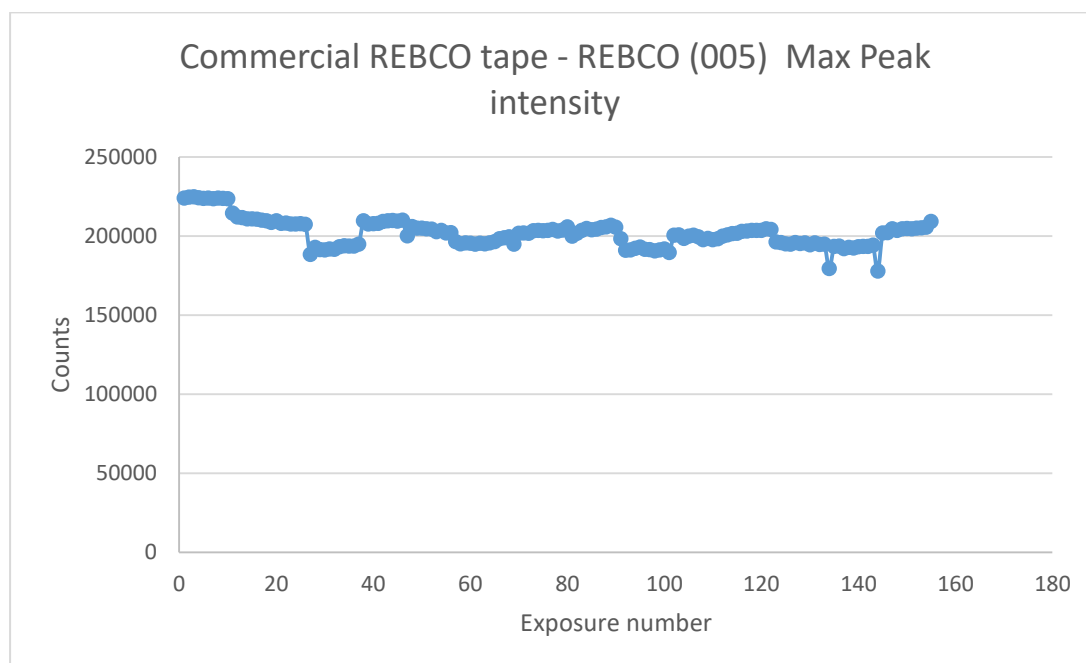


Figure 3.29 Maximum peak intensity of REBCO (005) of commercial tape vs exposure number.

Figure 3.29 represents maximum peak intensity of the REBCO (005) peak highlighted in the ROI as shown in Figure 3.30 which is a XRD pattern of a single exposure taken from the experiment. It can be clearly seen that the maximum variation in the count intensity observed across the length 15 cm in length is only about 20 percent which is nominal and might be due to small variation in thickness or chemical composition across the length of the tape.

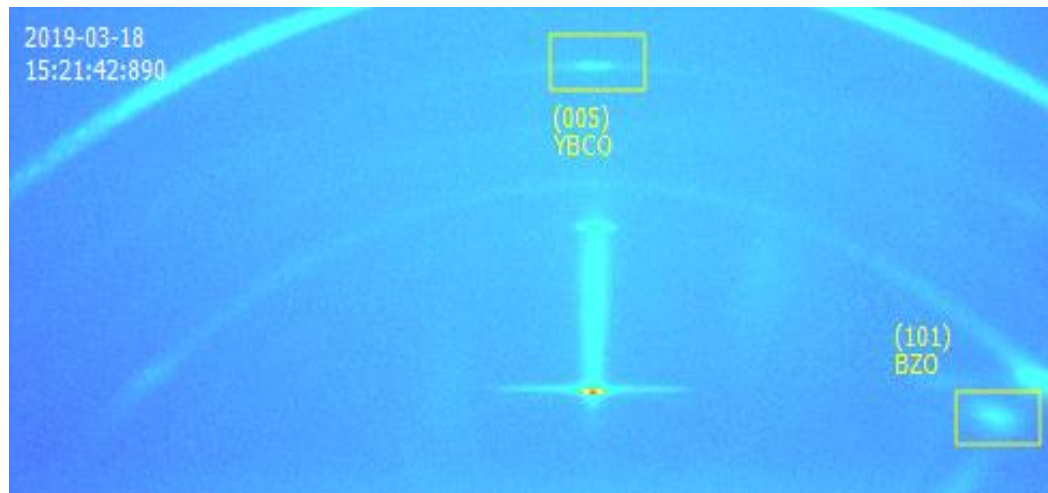


Figure 3.30 Snapshot of single XRD pattern obtained from commercial reference REBCO tape.

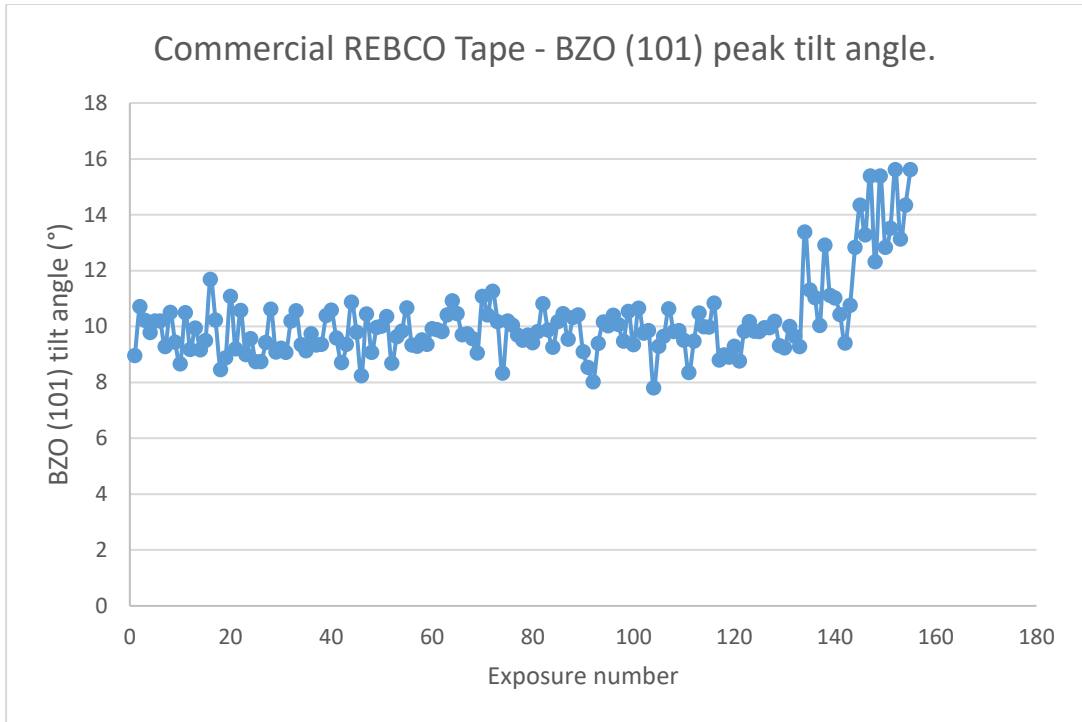


Figure 3.31 BZO (110) peak tilt angle of Commercial REBCO tape vs Exposure number.

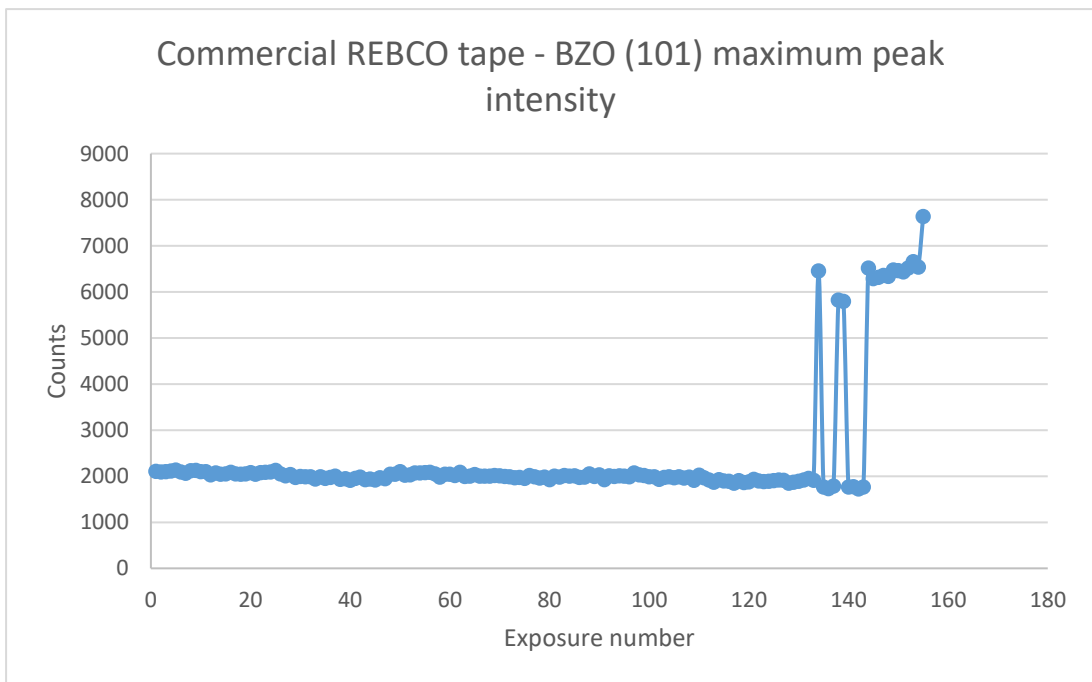


Figure 3.32 BZO (101) maximum peak intensity of Commercial REBCO tape vs Exposure number.

It can be seen from Figure 3.31 that the tilt angle that is reported by elliptical fitting to the BZO (110) peak stays relatively constant throughout the length of the tape. A variance

of 0.67 degrees was calculated in the peak tilt angle up to 140 exposures. A drift away from the nominal value is seen towards the end of the tape after about 140 exposures. A corresponding spike is also seen in the maximum peak intensity being recorded within the ROI. This was later diagnosed to be an issue with the fitting algorithm finding the wrong peak within the assigned ROI; REBCO (103) instead of BZO (101) was fitted since they are adjacent to each other and wrong values were reported as a result. The issue is explained in Figure 3.33 and Figure 3.34.

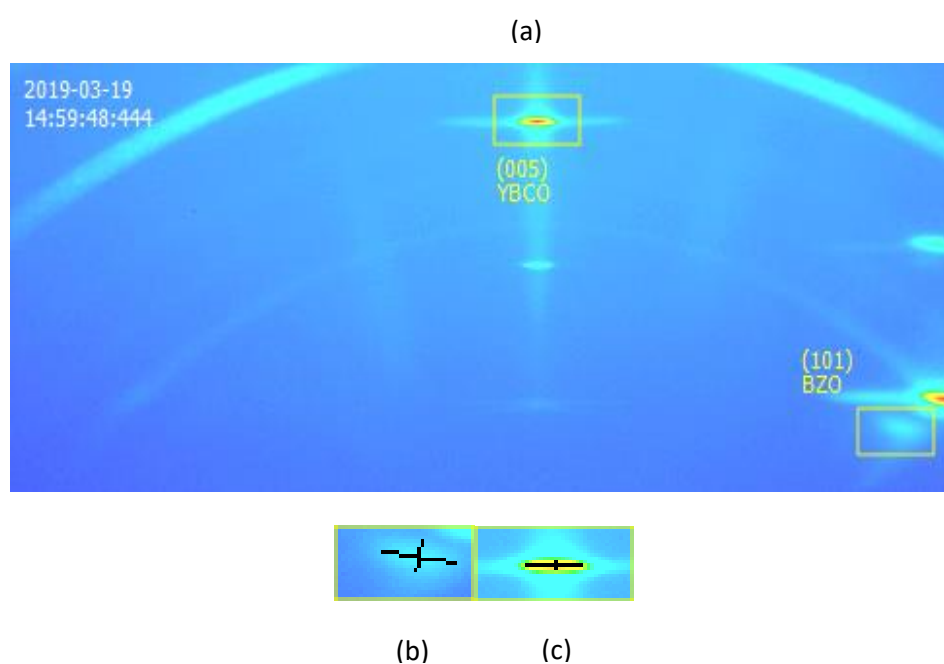


Figure 3.33 – Single exposure XRD pattern of a commercial REBCO tape at a point with nominal peak fittings. (a) XRD pattern (b) BZO (101) peak (c) REBCO (005).

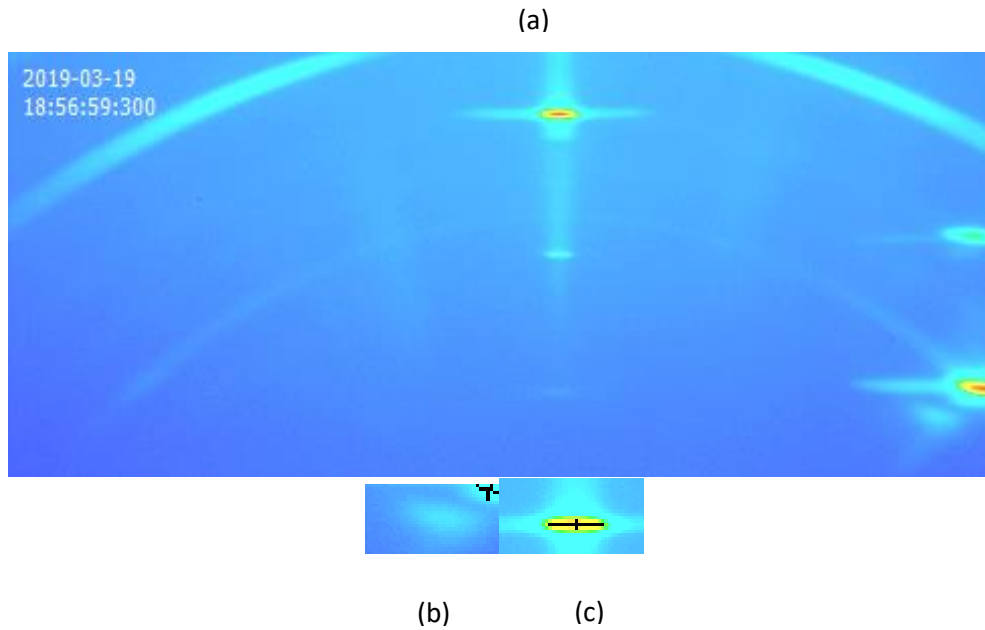


Figure 3.34 Single exposure XRD pattern of a commercial REBCO tape at a point near the end of the tape with wrong peak fittings. (a)XRD pattern (b) BZO (101) peak being fitted wrongly to REBCO (103) (c) REBCO (005) peak

Figure 3.33 shows a single screenshot of the software algorithm fitting peaks to both the ROIs and returning nominal values which are well within the expected range. Figure 3.34 shows a snapshot of the algorithm misfiring and finding the maximum intensity peak within the ROI; in this case, near the end of the tape, REBCO (103) is much stronger than BZO (101) and the elliptical pattern is fitted to the REBCO peak and wrong values are returned. This was then addressed by readjusting and redrawing the ROI to capture mainly the BZO (101) peak as shown in Figure 3.35. An upgrade has also been added to the software that allows the user to draw elliptical ROIs which are more useful and flexible for capturing full peak information especially in regions with overlapping or strong adjacent peaks.

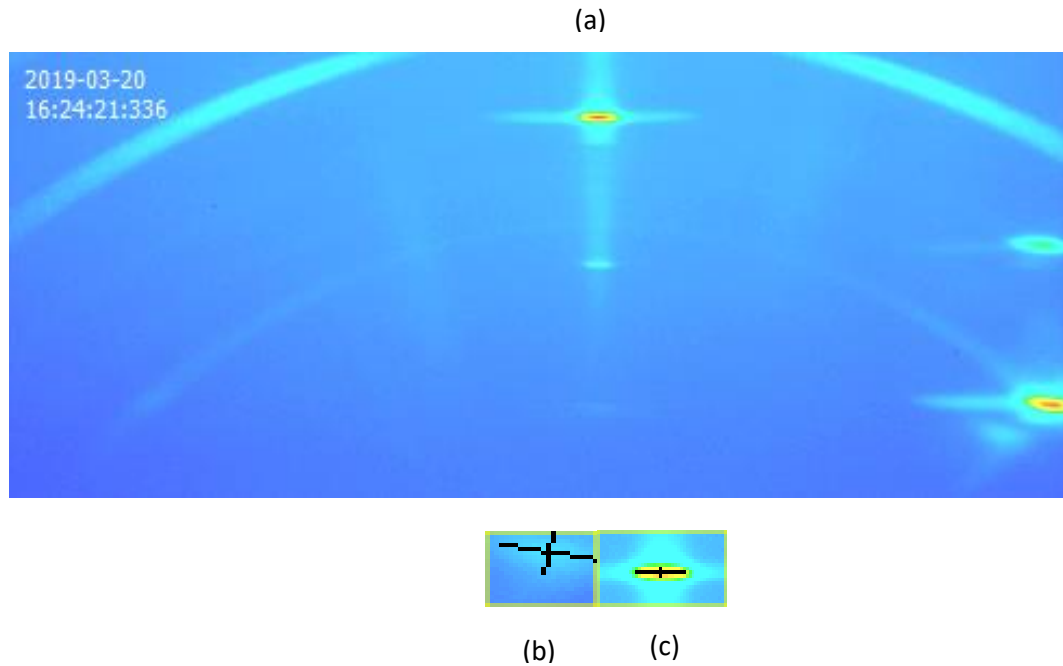


Figure 3.35 Single exposure XRD pattern of a commercial REBCO tape at a point near the end of the tape with nominal peak fittings after adjusting the ROI (a)XRD pattern (b) BZO (101) peak (c) REBCO (005) peak.

Four points were captured near the end of the commercial REBCO tape with the reconfigured conditions as shown in Figure 3.36 - Figure 3.38. The calculated variance in the peak fitting tilt angle is 2.55 degrees which is substantially higher than the earlier reported value of 0.67 degrees. This was because of maximum peak intensity dropping from an average of nearly 2000 counts to 1500. So, maintaining strong count intensity is an important parameter to reduce oscillation in the peak fitting tilt values. Increasing oscillation in these values can also act as an important alarm parameter for the operator to check processing conditions since that might be an indication of increasing non-homogeneity in the microstructure or chemical composition of the tape.

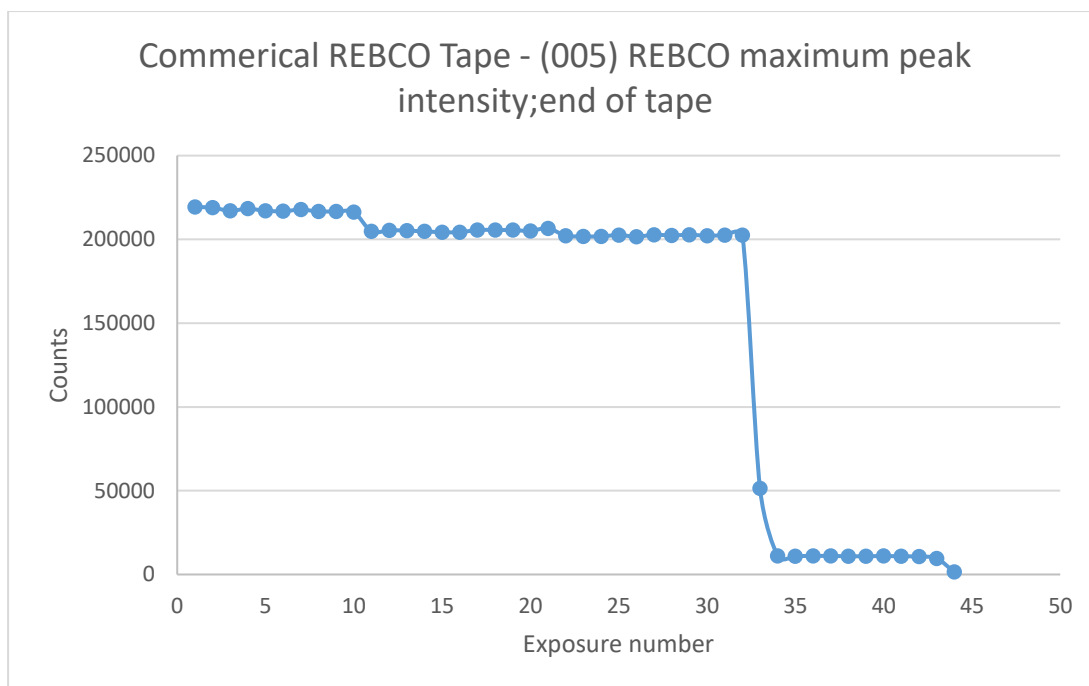


Figure 3.36 Maximum peak intensity of REBCO (005) of commercial REBCO tape vs exposure number for the last 4 points on tape.

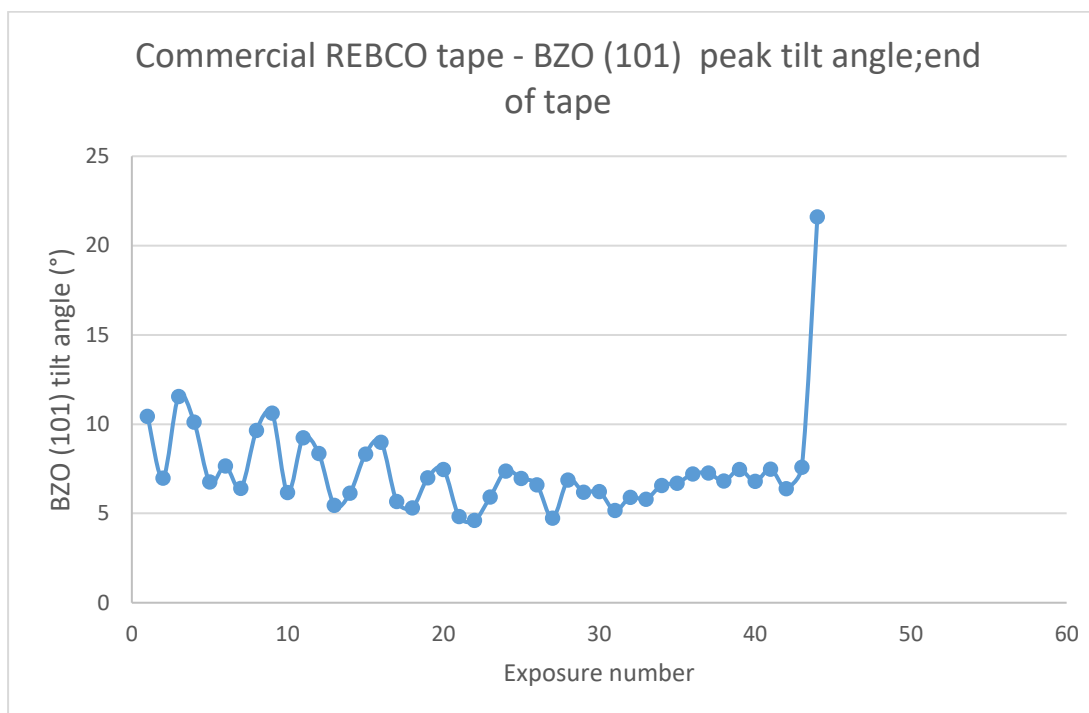


Figure 3.37 Tilt angle of BZO (101) peak of commercial REBCO tape vs exposure number for the last four points on tape.

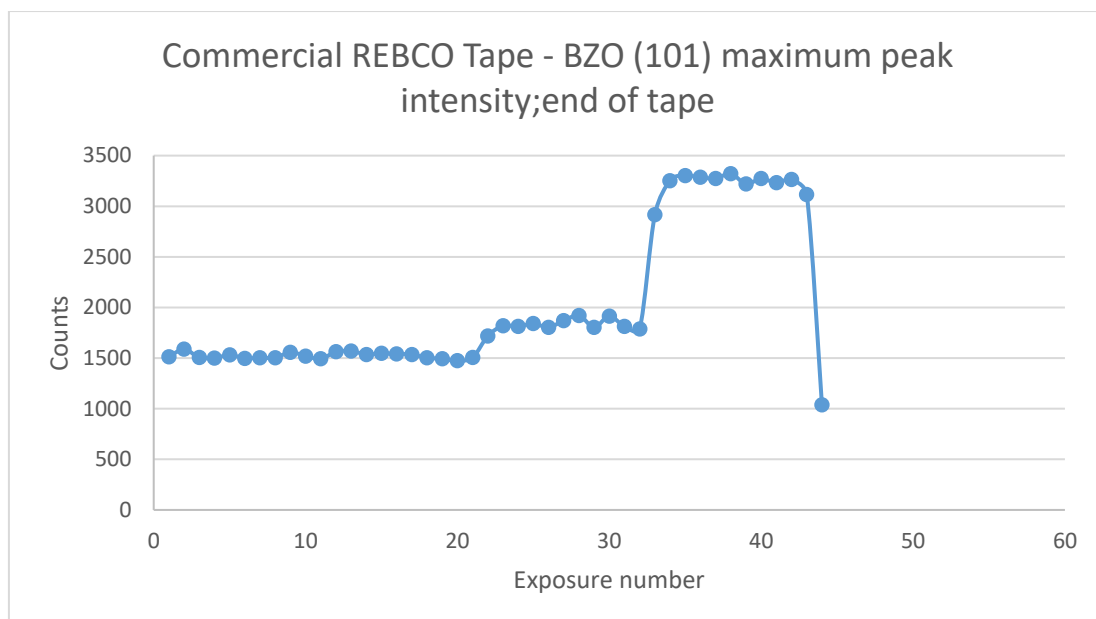


Figure 3.38 Maximum peak intensity of BZO (101) vs exposure number.

It should be mentioned at the outset that the objective of these experiments was to create a map along the entire length of the tape that could be correlated with data obtained from the ICP and PPMS by studying different sections of tape that exhibited significant differences in terms of their streaking angles. By creating a structural map of the entire tape along the length, important relationships could be obtained by correlating the microstructure with critical current, magnetic performance properties and chemical composition. For example, a wealth of data has been accumulated in this study by creating a map of the rare earth oxide peak intensities along the entire length of the tape which has been strongly correlated with pinning in the a-b plane and potentially affecting the BZO nanorod growth along the c axis [101]. Systematic studies of variations in angular-dependent magnetic field critical current carrying capacity could be conducted using this data in the future.

Table 3.3 lists out all the samples that were used for the 2D GADDS XRD studies with their nominal compositional information along with the normalized magnetic I_c measured using PPMS.

Table 3.3 – Sample ID, nominal compositional values in atomic percentage measured using ICP, (Ba+Zr)/Cu ratio and normalized magnetic I_c @ 77 K, 0 T.

Sample ID	Cu	Y	Zr	Ba	Gd	(Ba + Zr)/Cu	Normalized Magnetic I_c @ 77 K, 0T
Commercial XRD Reference	50.9	8.8	0.9	31.2	8.3	0.6000	414.12
PM 218 8	47.0	8.2	0.9	34.9	9.0	0.7611	195.92
PM 221 16	45.9	10.7	1.0	32.0	10.4	0.7191	276.35
PM 221 4	46.2	11.8	0.6	30.0	11.4	0.6611	707.22
PM 223 2	44.8	9.7	1.4	33.9	10.2	0.7868	226.89
PM 224 6	46.7	8.9	0.5	34.4	9.5	0.7454	510.68
PM 224 7	46.7	9.0	0.5	34.3	9.5	0.7459	493.68
PM 224 18	44.9	8.9	1.4	35.4	9.4	0.8214	59.98
PM 224 19	45.0	8.6	1.3	36.0	9.0	0.8294	98.46

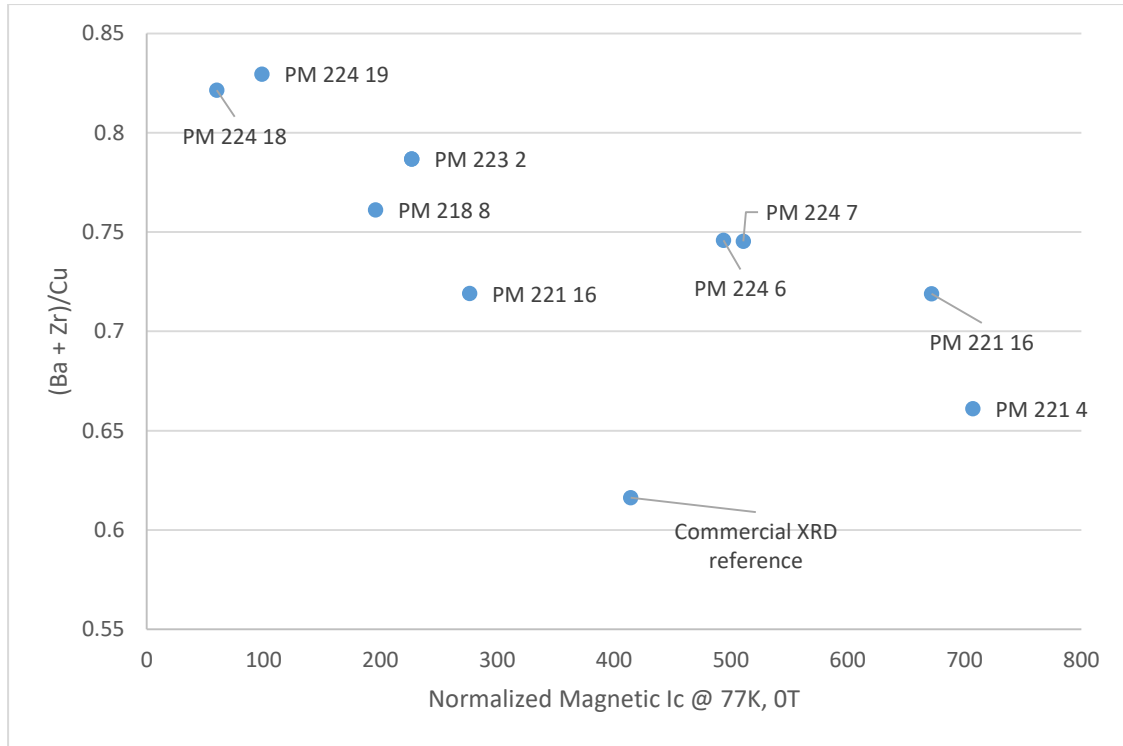


Figure 3.39 Plot of $(Ba + Zr)/Cu$ vs Normalized magnetic I_c @ 77K, 0T measured using PPMS.

It can be clearly seen from Figure 3.39 that the compositional ratio of $(Ba+Zr)/Cu$ has a strong correlation with the magnetic I_c measured at 77 K, 0T. The commercial XRD reference sample however stands out from this trend. It should be pointed out that the commercial XRD reference sample is only $1.5 \mu m$ thick as opposed to all the other PM samples which are $4.5 \mu m$ thick.

Correlations have been established with in-plane and out of plane texture of REBCO tape with self-field I_c at 77 K [84]. However, that was not the goal of this study. The goal of this thesis work is to find all the potential metrics of the REBCO tape that can be correlated with XRD data that can be obtained inline.

PM 221 4 was the first AMOCVD tape to be measured using the inline 2D GADDS XRD.

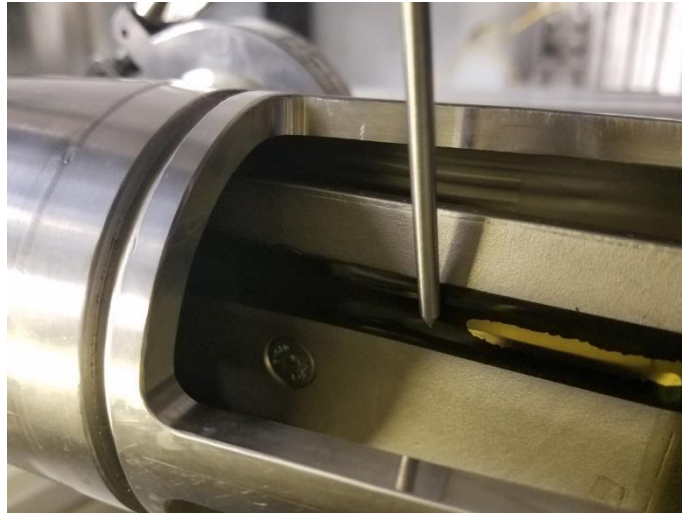


Figure 3.40 Photo of PM 221 4 tape showing delaminated section. Measurements were performed starting right outside the delaminated section.

Unfortunately, this tape suffers from extensive delamination issues despite having high self-field I_c . So it was decided to start the measurements right outside the delaminated section and sets of 10 exposures were taken at every single point of measurement each spaced roughly 0.5 cm apart for this tape. This will provide important structural information across the length of the tape. Figure 3.41 – 3.44 exhibit the typical array of peaks that were captured along the entire length of the tape in order to construct a full microstructural map of the tape.

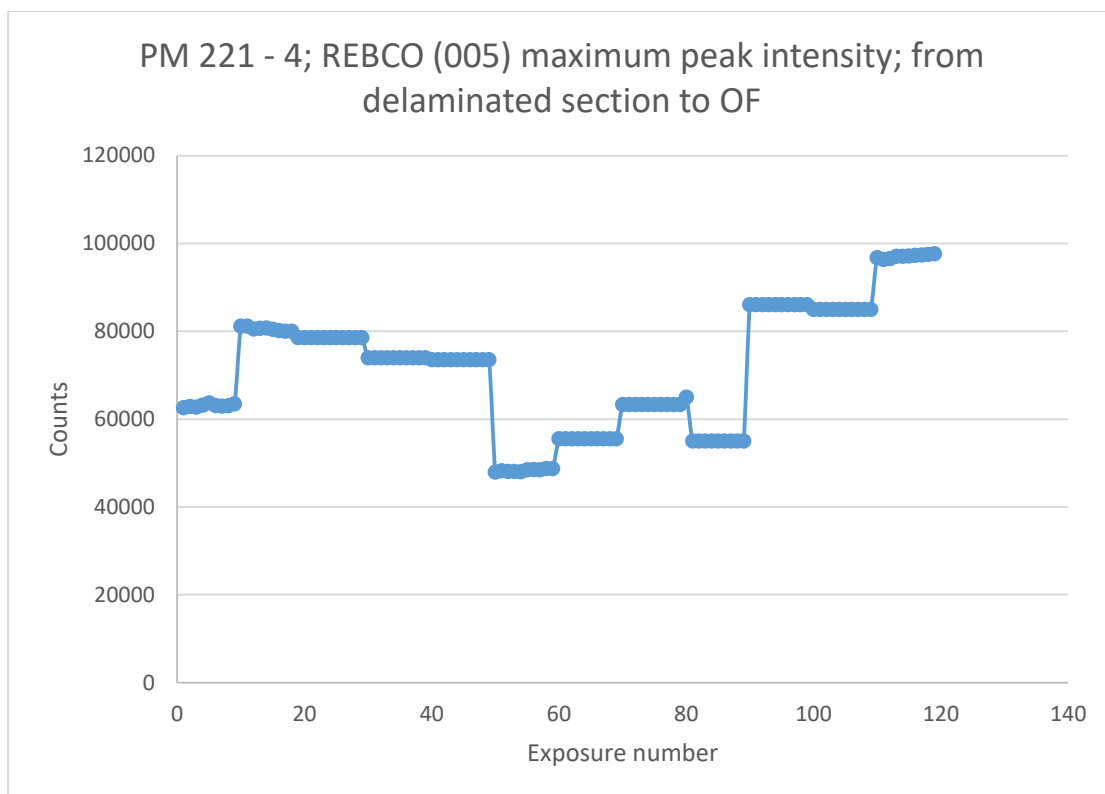


Figure 3.41 PM 221 4 – REBCO (005) maximum peak intensity vs exposure number

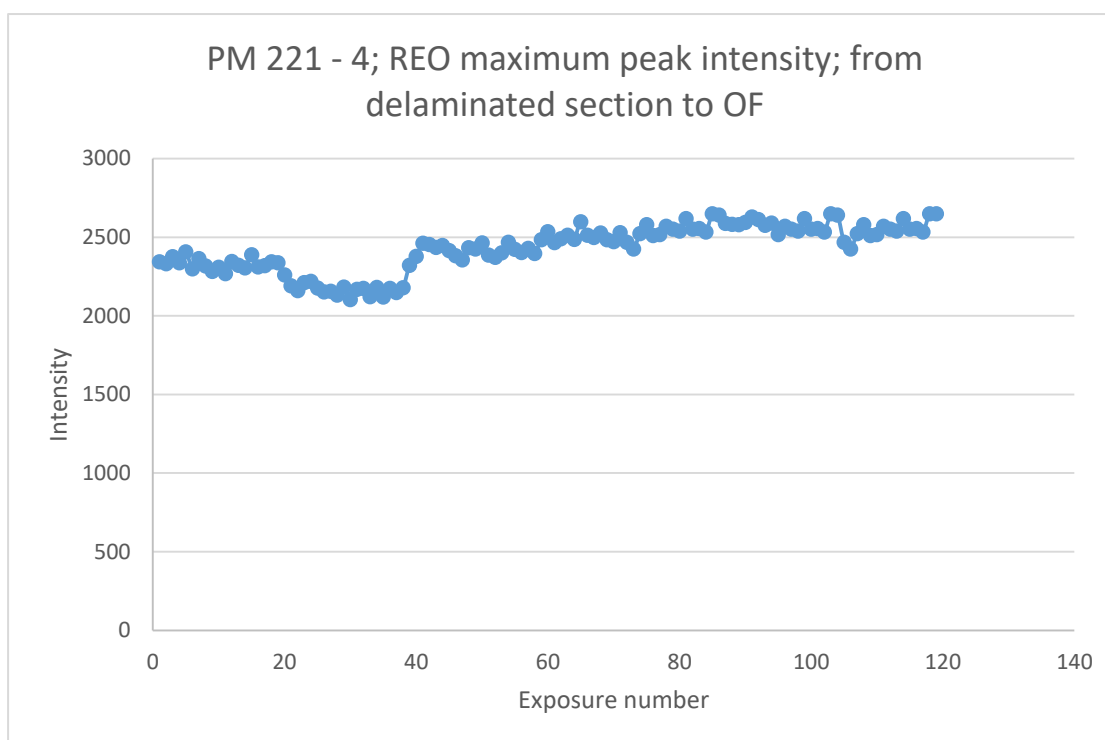


Figure 3.42 PM 221 4 – REO (400) maximum peak intensity vs exposure number

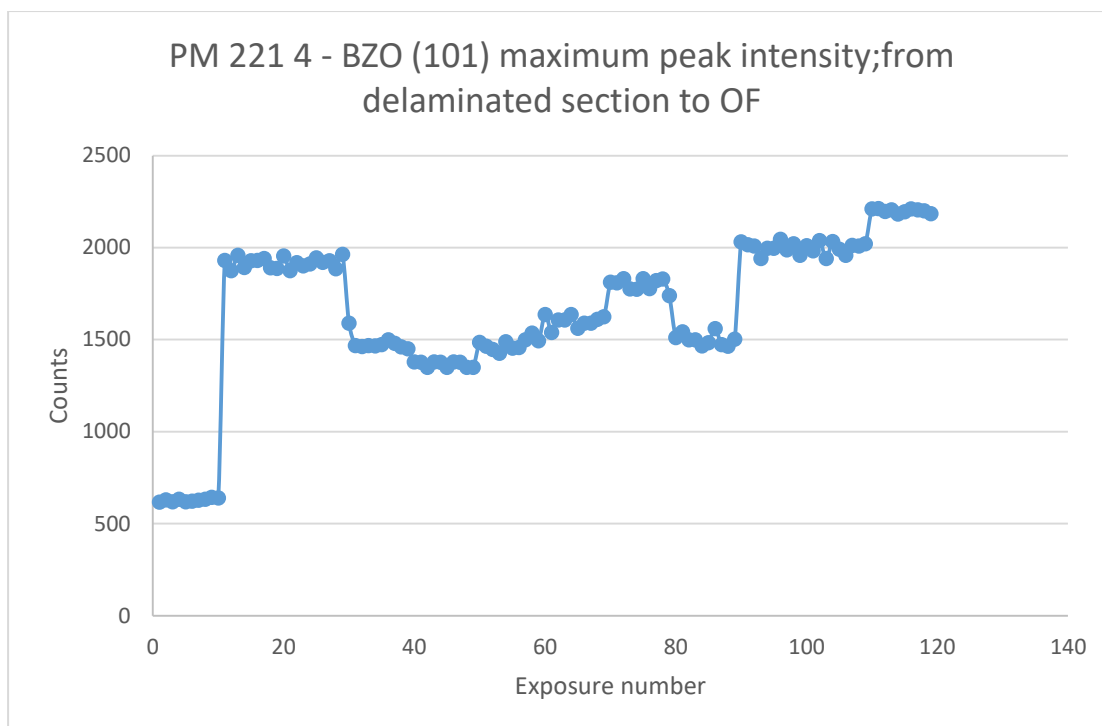


Figure 3.43 PM 221 4 - BZO (101) maximum peak intensity vs exposure number.

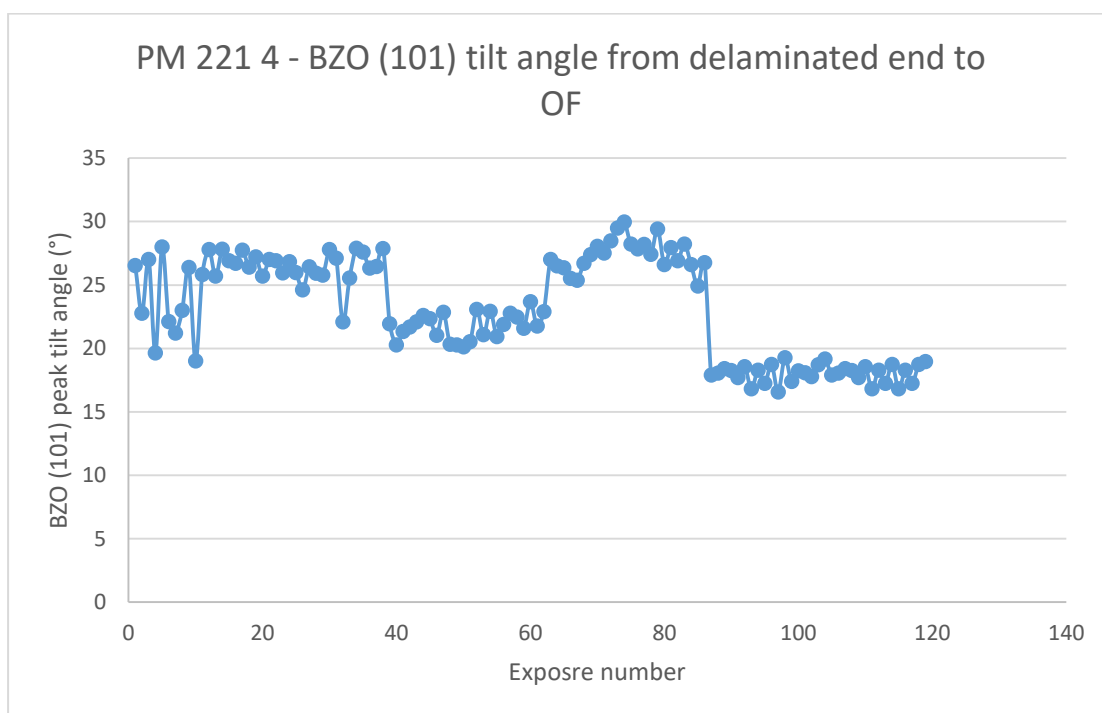


Figure 3.44 PM 221 4 - BZO (101) peak tilt angle intensity vs exposure number.

Out Far (OF) is designated as one of the end points and refers to the exit end of the tape in the Advanced MOCVD reactor. This tape exhibits significant non uniformity in its

measured crystalline structural properties in terms of both the intensity and peak tilt angle variation of BZO(101) along its length and no definitive correlation could be found between variations in intensity and the tilt angle for any of the tapes except for subtle variations in standard deviation of the tilt angle fitting as explained in Figure 3.37. The maximum peak intensity of REBCO (005) also shows substantial variation along the length and no direct correlation exists in terms of intensity variation between the primary REBCO phase and the secondary BZO and REO phases on this tape. A section of the tape in the middle was cut and measured in PPMS. Different sections of this tape were also used for PPMS measurements to study intra tape variance of the BZO (101) streaking angle with PPMS and ICP data. Since some parts of the sample got delaminated, thickness studies were not conducted on this sample. Figure 3.45 is a SHPM profile of the self-field I_c measured at 77K, 0 T.

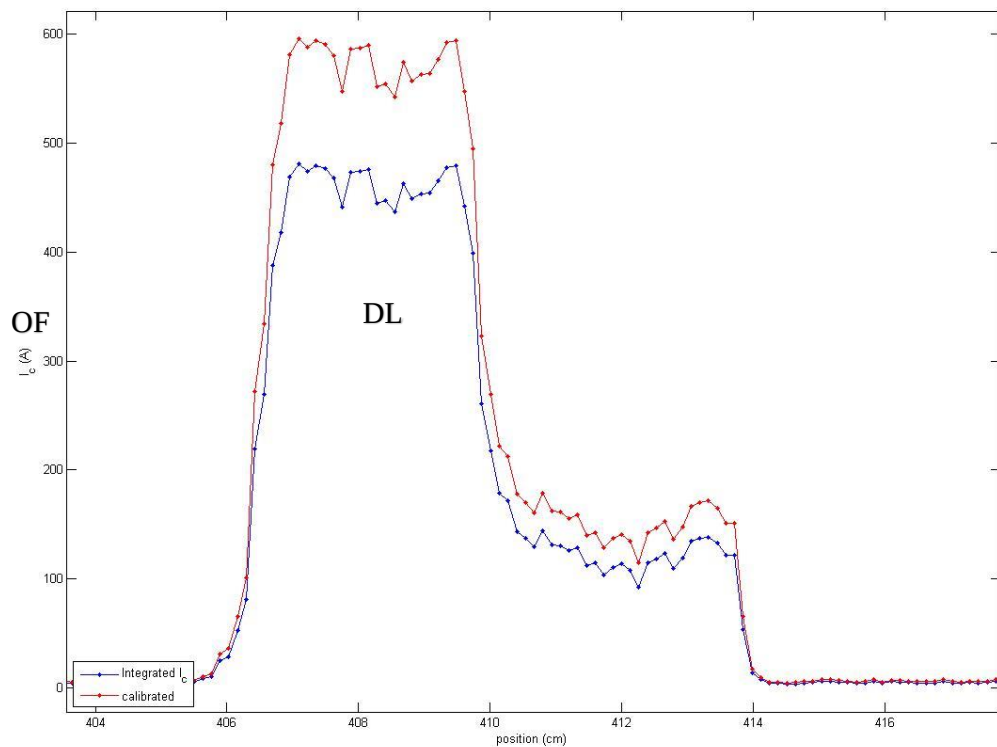


Figure 3.45 Measured I_c of PM 221 4 tape using SHPM. The delaminated end (DL) and OF ends of the tape are marked on the graph. Integrated I_c is the critical current measured using the SHPM, calibrated I_c refers to critical current values calibrated to transport I_c values measured at 77 K.

PM 223 2 was the next tape to be studied using the inline 2D GADDS XRD. Out Far (OF) is again designated as one of the end points and the other end is designated as TC which refers to the location of the approximate center of the Advanced MOCVD reactor. The experimental conditions were kept the same for all the tapes going forward – 10 exposures per point, each point equispaced roughly 0.7 – 0.8 cm apart with a 1mm slit and 90 second dwell time.

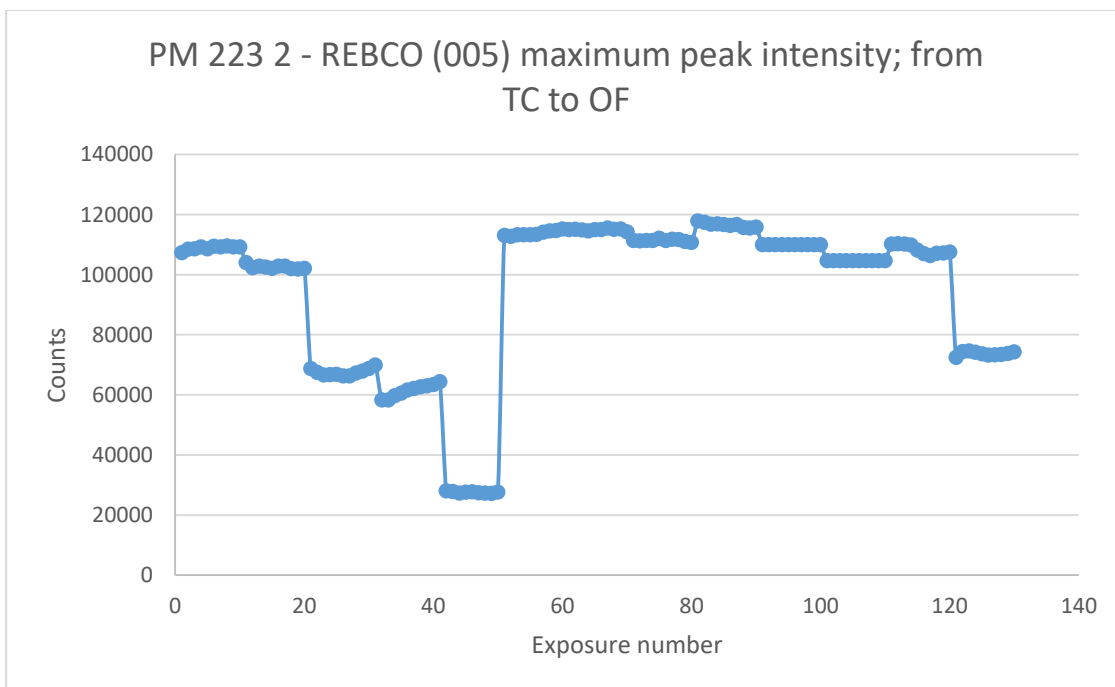


Figure 3.46 PM 223 2 – REBCO (005) maximum peak intensity vs exposure number.

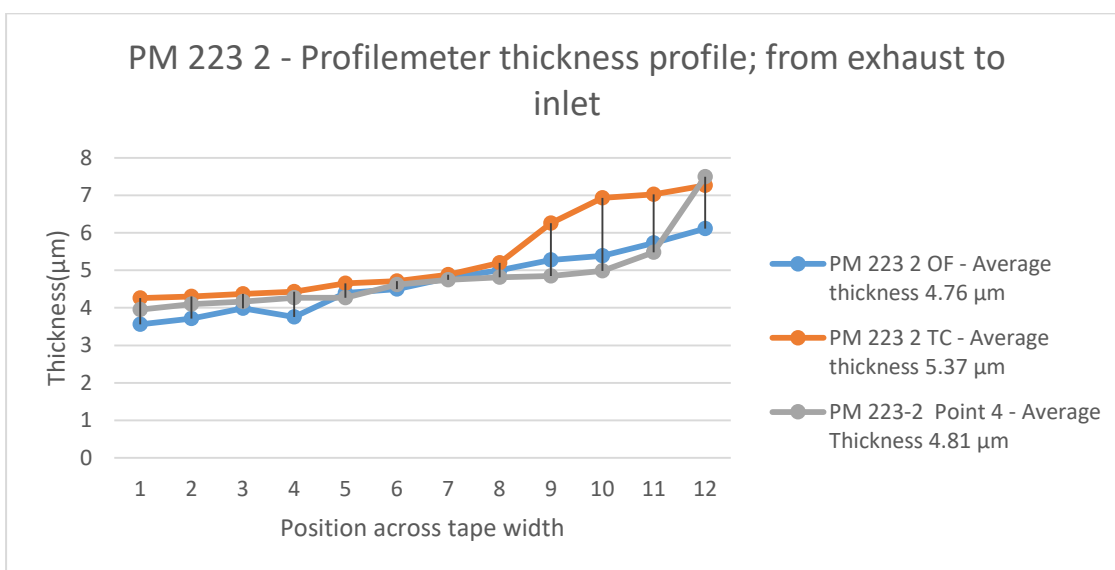


Figure 3.47 Thickness profile across the width of PM 223 – 2 samples.

By measuring the thickness of the REBCO film across the width at equispaced intervals using a profilometer, profiles of the thickness of the tape are obtained at different points along the length. The extreme end points in the width direction are ignored since they are dead zones of mostly a-axis grains so that nominal thicknesses can be compared. Measurement across the width was conducted to study the uniformity of the tape deposition across the width of the tape since there was a substantial variation in the thickness of the film grown by AMOCVD initially, which has since been addressed using a slanted top plate. Nevertheless, this is a useful metric to track since it can reveal information about homogeneity across the width of the tape and taken at different points along the length of the tape, gives a two dimensional perspective on the uniformity of the deposition process. In this case, a drop of nearly 30,000 counts is observed when moving from the TC region to the OF region. The average thickness of the film (averaged across the width of the film) measured on the profilometer drops from 5.37 μm to 4.67 μm . The calculated X-ray beam divergence on the tape is 5.5 mm at this incident angle with a 1 mm pinhole aperture. Although the tape is focused using the touch pointer on the center of the tape, due to camber in the motion of the tape, it is likely that the sampled region lies slightly to the left or right of the center line of the tape. So the average thickness of the tape is a more useful metric for comparing intensities.

Plotting the profilometer data, it can be clearly seen that the thickness variation along the tape length is small and not significant enough to explain the drops in the counts of maximum peak intensity of the REBCO (005) in Figure 3.45 especially moving from the TC end to point number 4 (exposure number 40 to 50) after which the counts come back to nominal levels again. Chemical compositional variations or formation of secondary phases along the length of the film can also be the reasons for these dropouts as opposed to variations in the thickness of the REBCO film. HRXRD scans were conducted at 4 points along the length to verify the information from the inline XRD. ICP MS characterization was also performed on the same samples.

- 1) Point 2 – point on the tape where exposures 20 – 30 were captured.
- 2) Point 3 – point on the tape where exposures 30 – 50 were captured.
- 3) Point 4 – point on the tape where exposures 40 – 50 were captured.
- 4) Point 5 – point on the tape where exposures 50 – 60 were captured.

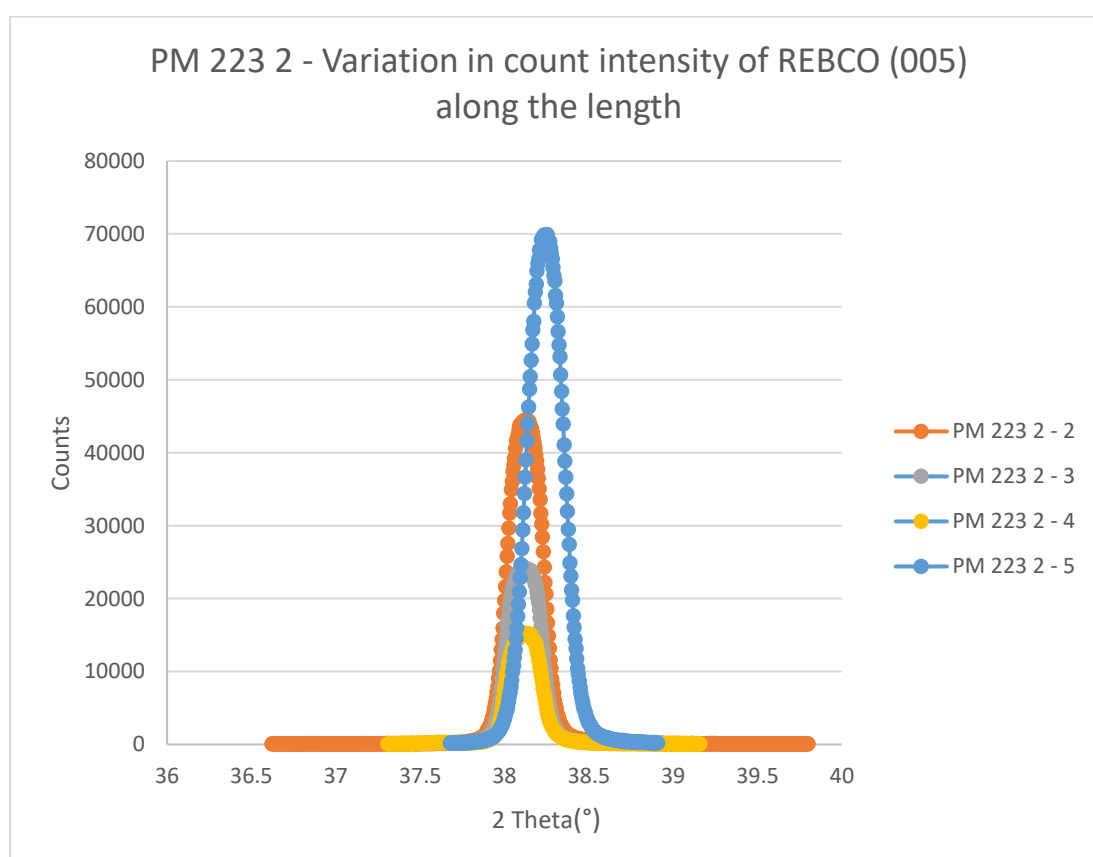


Figure 3.48 HRXRD measurement of REBCO (005) peak intensity of PM 223 2 along the length.

Figure 3.48 shows the variation in the intensity of the REBCO (005) peak along the length of the PM 223 2 sample. It's remarkably consistent with the results shown in Figure 3.46 considering that the ratio of the intensity of point 2 to point 5 and point 4 to point 5 is almost exactly in the ratio that is seen in Figure 3.46.

Rare earth oxide grains were however not scanned separately and was captured as part of a larger theta – 2 theta symmetrical scan in Figure 3.49 and since BZO (101) is off

axis and is visible directly only in GADDS, its data is not available with HRXRD. However the trend of the data follows the same order and if sufficient dwell time is given within the 2 theta range, similar ratios can be obtained.

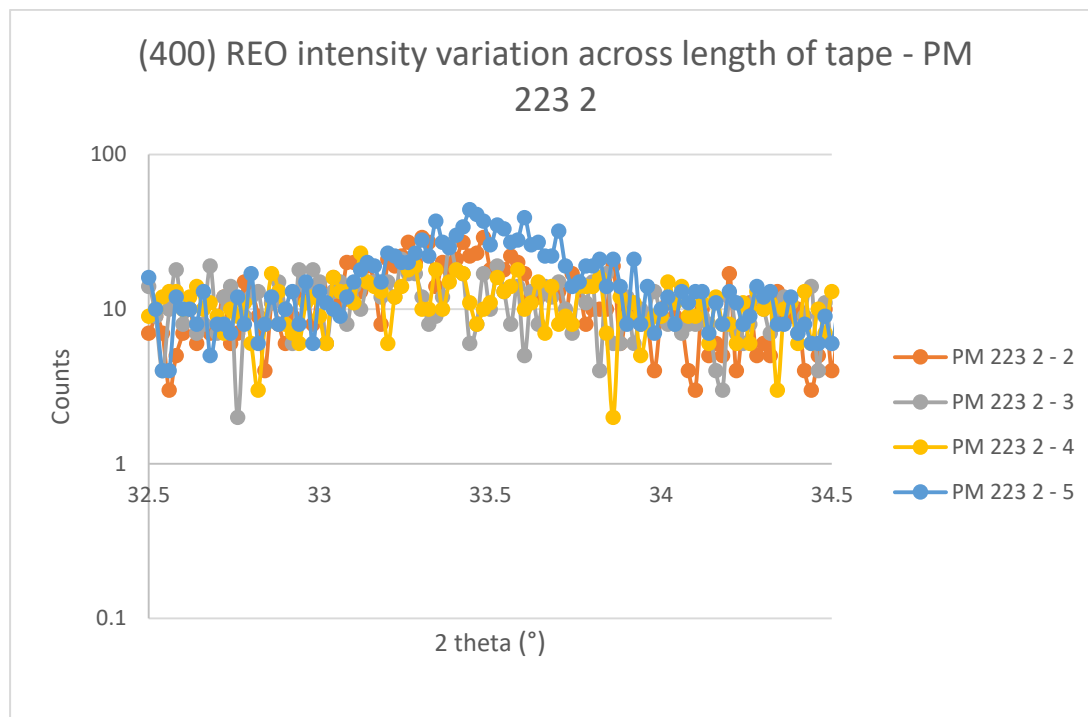


Figure 3.49 HRXRD measurement of REO (400) peak intensity of PM 223 2 along the length.

It is clear from Figure 3.47 and Figure 3.48 that the trend that is being displayed by the inline XRD is real. Geometrical alignment issues were addressed early on with the XRD setup having a stable 2D platform on which the tape is stabilized under tension as shown in Figure 3.50 so that noise is not induced due to the mechanical motion of the setup.

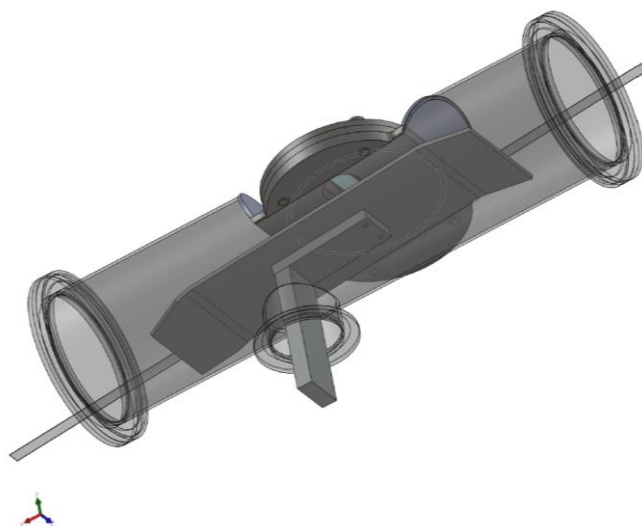


Figure 3.50 CAD rendering of the new platform for 2D GADDS XRD with feedthrough.

Table 3.4 displays the chemical composition of the tapes obtained through performing ICP analysis on the same exact region where the HRXRD measurements were conducted.

Table 3.4 – ICP MS analysis of PM 223 samples at the exact same region of measurement as HRXRD. All compositions given in atomic percentage.

Sample ID	Cu	Y	Zr	Ba	Gd
PM 223 2 - 2	46.2	9.6	1.3	33.0	9.9
PM 223 3 - 3	46.3	9.7	1.2	32.9	9.9
PM 223 4 - 4	46.9	9.3	1.3	33.2	10.0
PM 223 5 - 5	46.6	9.8	1.3	32.2	10.0

A slight increase in copper and in barium is seen at point number 4 but apart from that, no other precursor elemental concentration is seen to vary drastically.

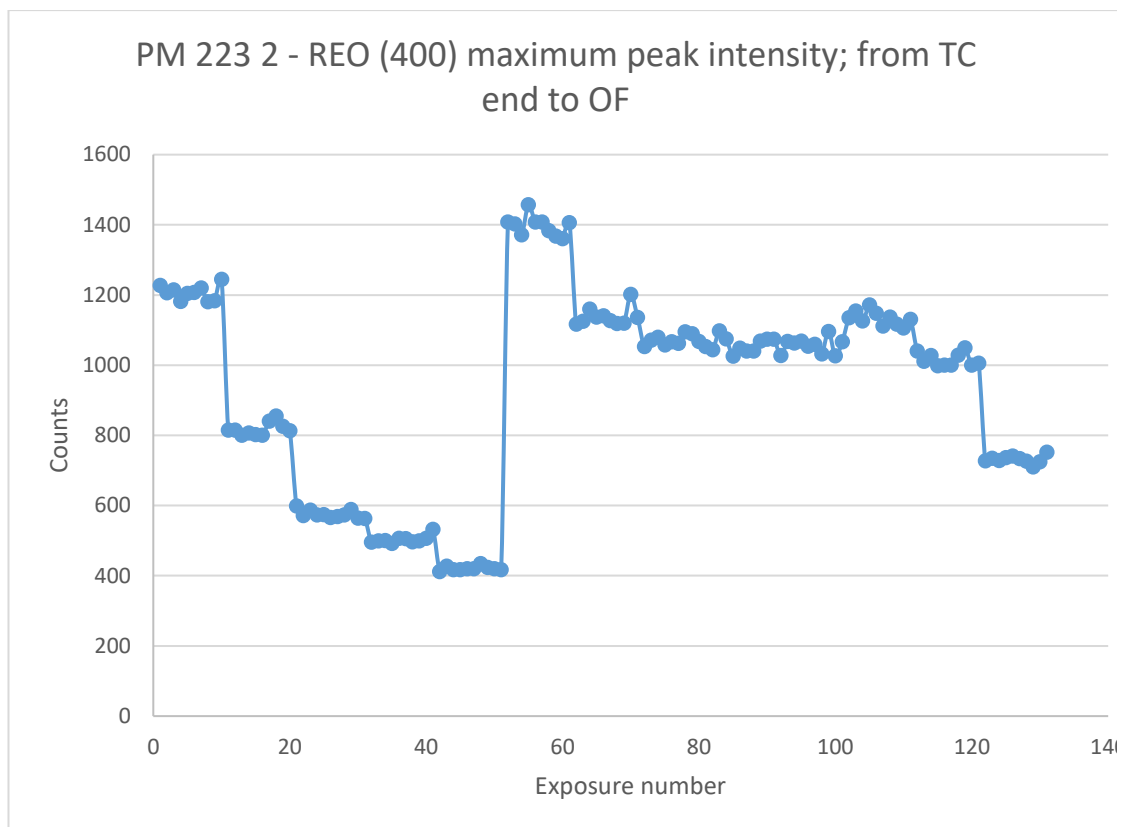


Figure 3.51 PM 223 2 – REO (400) maximum peak intensity vs exposures.

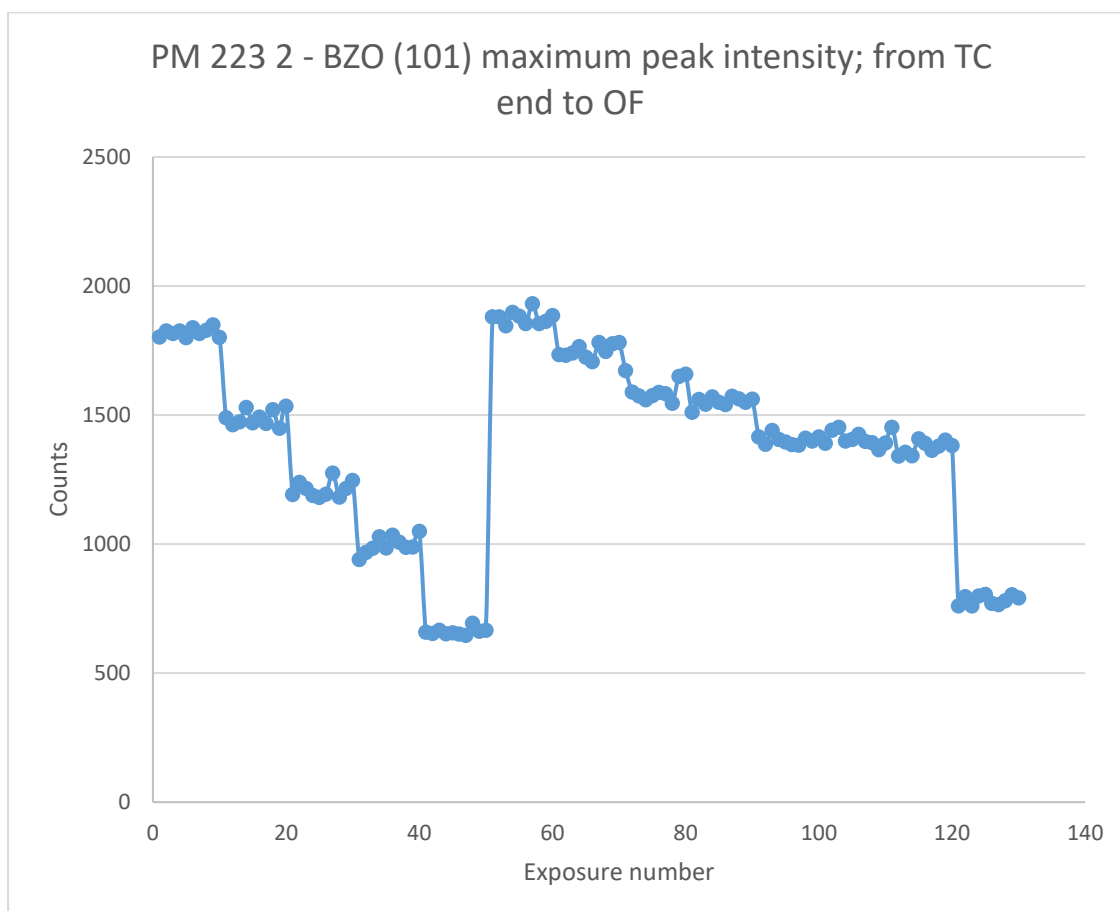


Figure 3.52 PM 223 2 – BZO (101) maximum peak intensity vs exposure number.

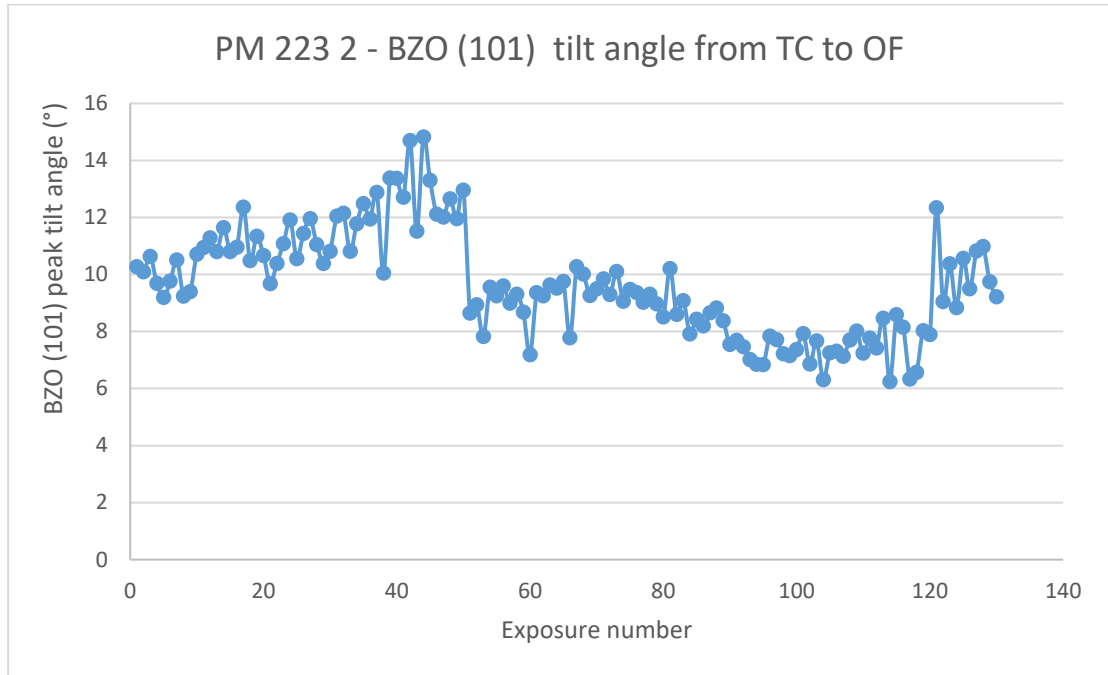


Figure 3.53 PM 223 2 – BZO (101) peak tilt angle vs exposure number

The decrease in the counts of each crystal phase with no major change in chemical composition more than likely points to a localized region on the tape where microstructural degradation has occurred due to hotspots. This can help explain the sharp drop in I_c seen from the TC side with a maximum of 180 A at 397 cm position in Figure 3.54 to a minimum value of 120 A at 396 cm position. The I_c hovers around that value for another 2 cm before rising back up again at 394 cm position. Five exposures have been captured between these two points which covers a span of 4 cm approximately. Monotonic decrease in intensity has been captured through a series of discrete snapshots mapping out a local region of degradation. Defining numerical relationships between a multivariate function of XRD like intensity and a complex superconducting parameter like I_c (which has already been established to be a function of composition also in Figure 3.39) is bound to be fraught with errors but in the context of a quick in-line technique capable of mapping out localized areas of degradation, it can provide invaluable data in an *in-situ* fashion.

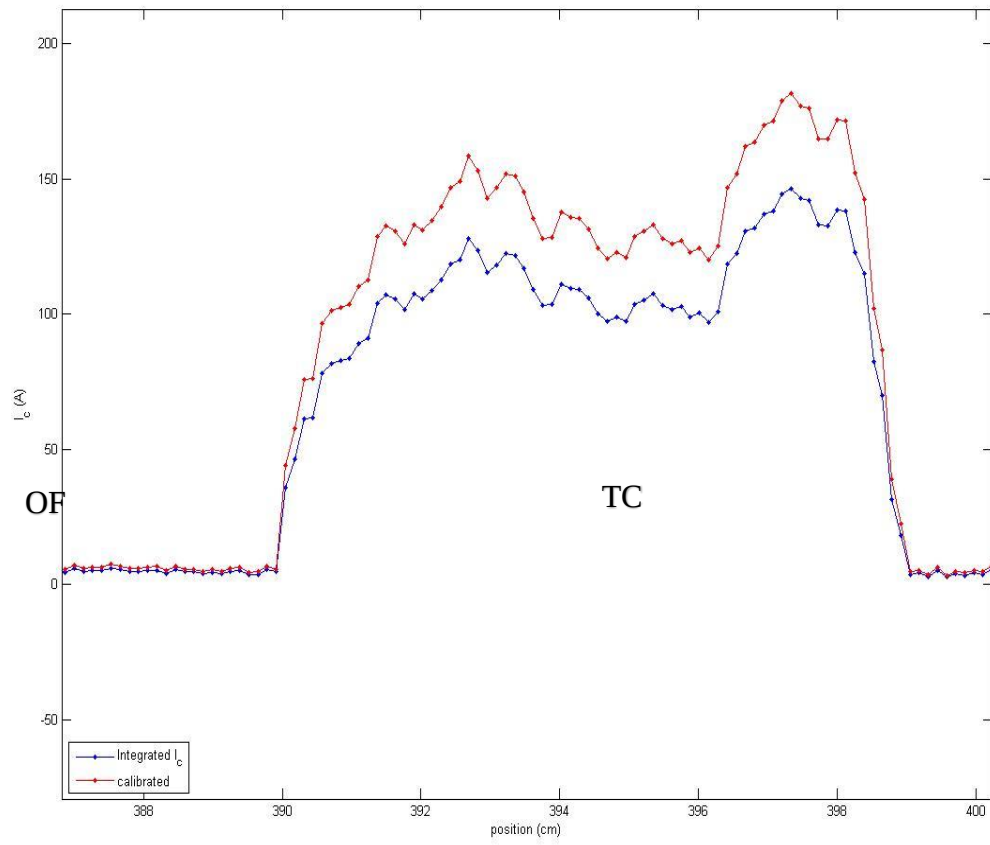


Figure 3.54 Measured I_c of PM 223 2 tape using SHPM. The OF and TC ends of the tape are marked on the graph.

The intensity data could be correlated with the thickness of the films in some cases; particularly for tapes that exhibit a sharp drop from a smaller region closer to OF and then reaches a nominal values which stays consistent throughout the length of the tape. This behavior is seen on some but not on all the tapes. Unlike the slow monotonic decrease in intensity over length that was discussed earlier, this is a singular sharp drop off in primarily the REBCO phases but not necessarily in all the other phases. PM 224 6 and PM 224 7, both of which were processed under similar conditions, exhibited this type of behavior. The goal of comparing tapes which were processed under similar conditions was to examine if the instrument is capable of discerning fine differences in the physical structure of these tapes and if not, check the reproducibility and replicability of these measurements across two tapes which were processed under very similar conditions.

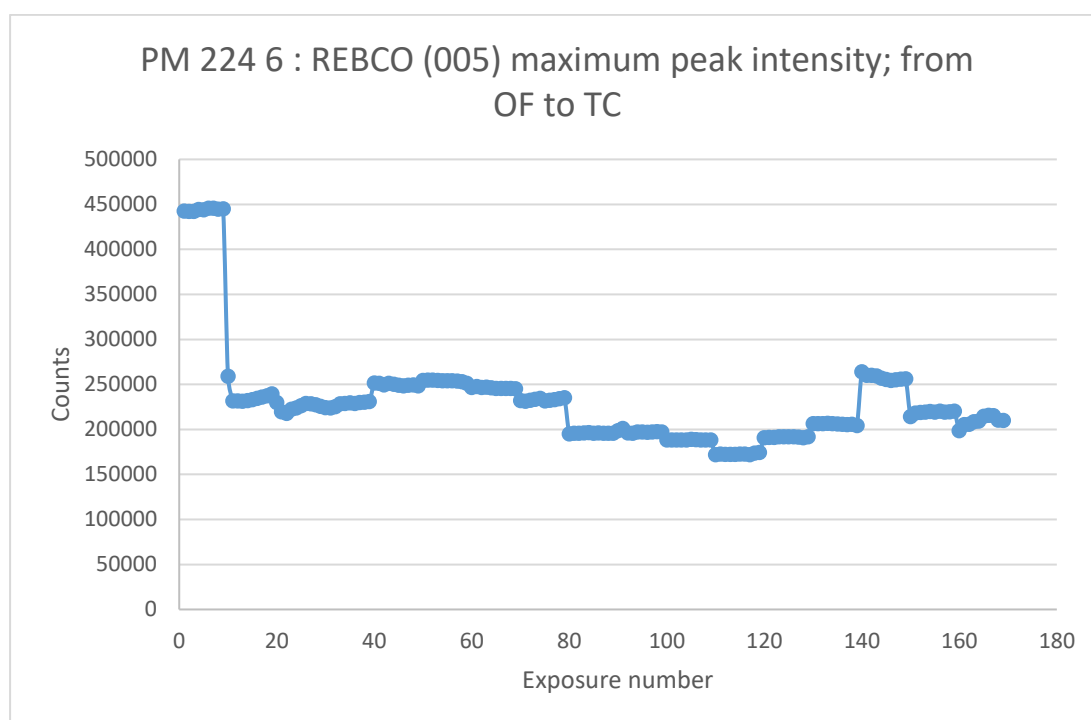


Figure 3.55 PM 224 6 – REBCO (005) maximum peak intensity vs exposure number.

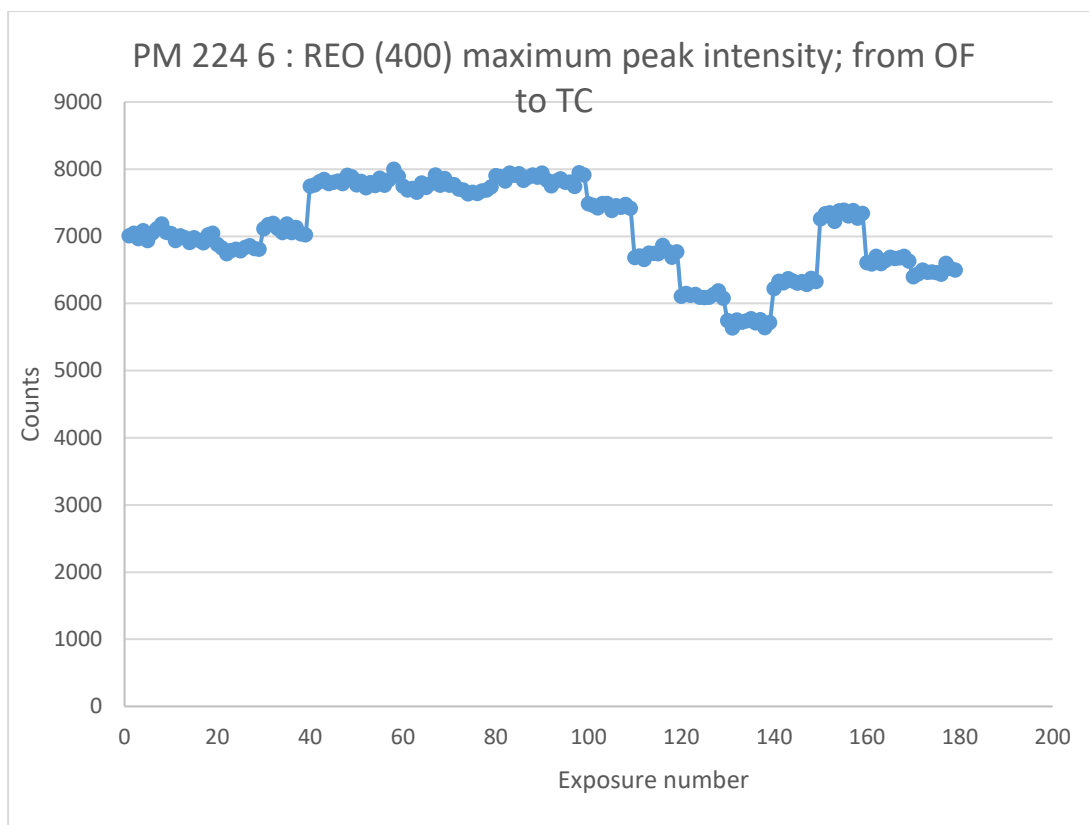


Figure 3.56 PM 224 6 – REO (400) maximum peak intensity vs exposure number

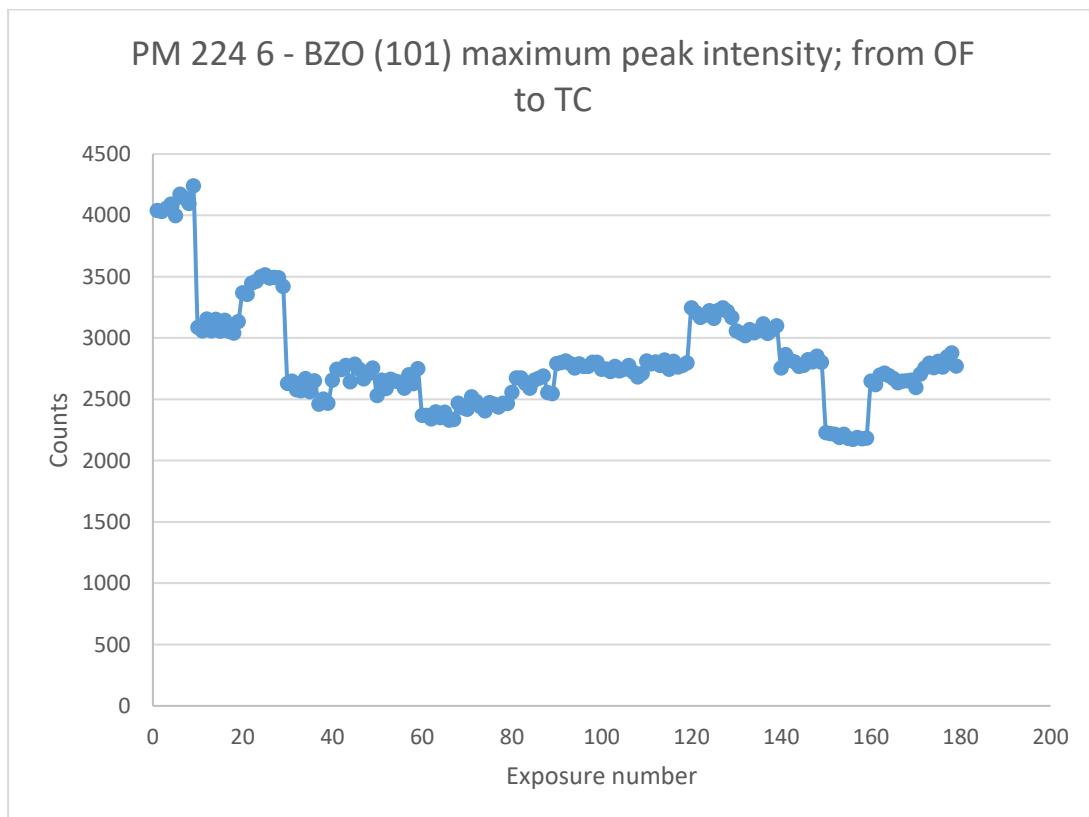


Figure 3.57 PM 224 6 – BZO (101) maximum peak intensity vs exposure number

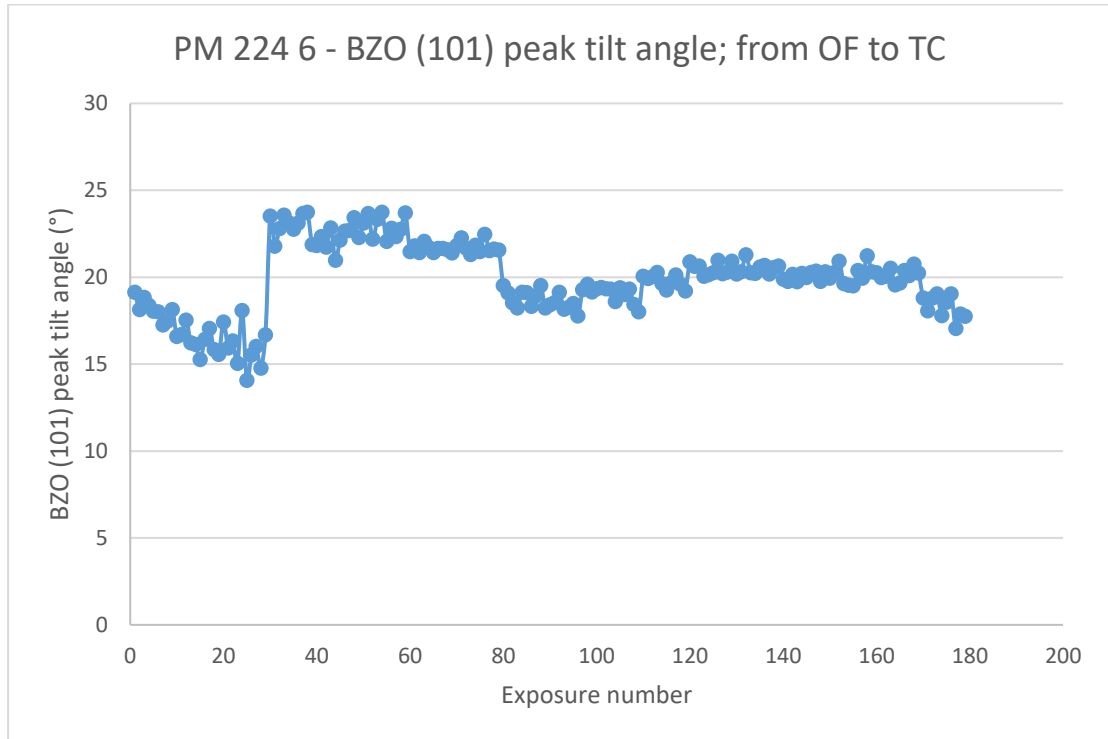


Figure 3.58 PM 224 6 – BZO (101) peak tilt angle vs exposure number

This particular tape exhibits a standard deviation of 2.03 in the BZO peak tilt angle across the length with the an average value of 19.89 degrees. The number of counts of the maximum peak intensity of the REBCO (005) peak drops sharply moving from point 1 (0 – 10 exposures) to point 2 (10 – 20 exposures) in Figure 3.54 and the BZO (101) peak also shows a similar trend in Figure 3.57 but the same drop is not seen in Figure 3.56 tracking the changes in the number of counts of peak intensity of the REO (400) peak. Correlation of the streaking angles with compositional variance across the length and magnetic field performance measured using the PPMS will be reported later in this disseration to provide insight into the triangulation of composition- microstrucuture – properties relationships. The SHPM of PM 224 – 6 is shown in Figure 3.59 with the OF and TC ends marked.

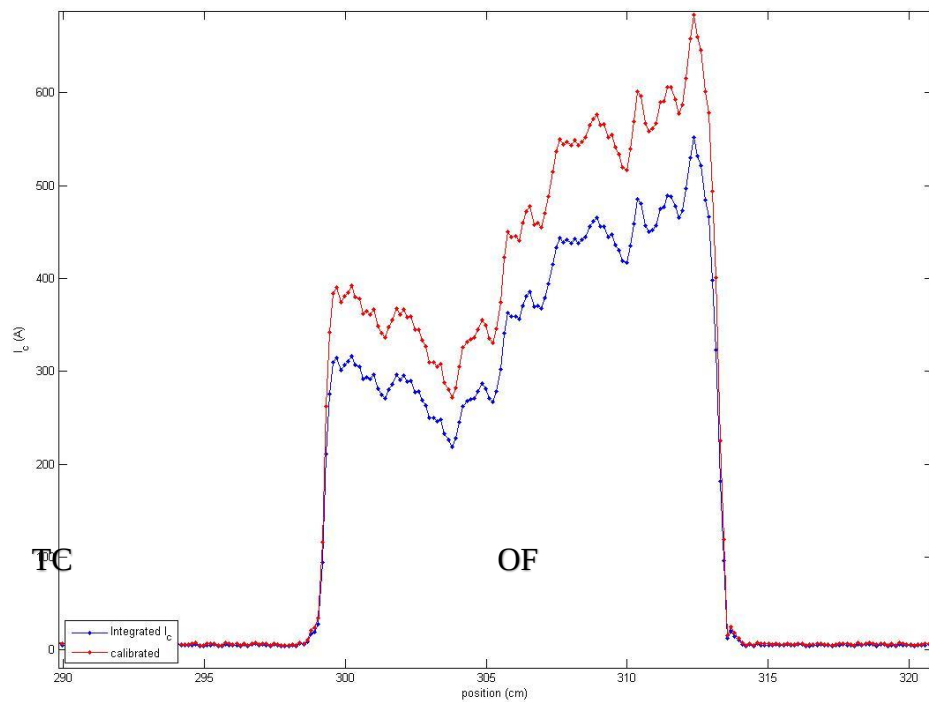


Figure 3.59 Measured I_c of PM 224 6 tape using SHPM. The OF and TC ends of the tape are marked on the graph.

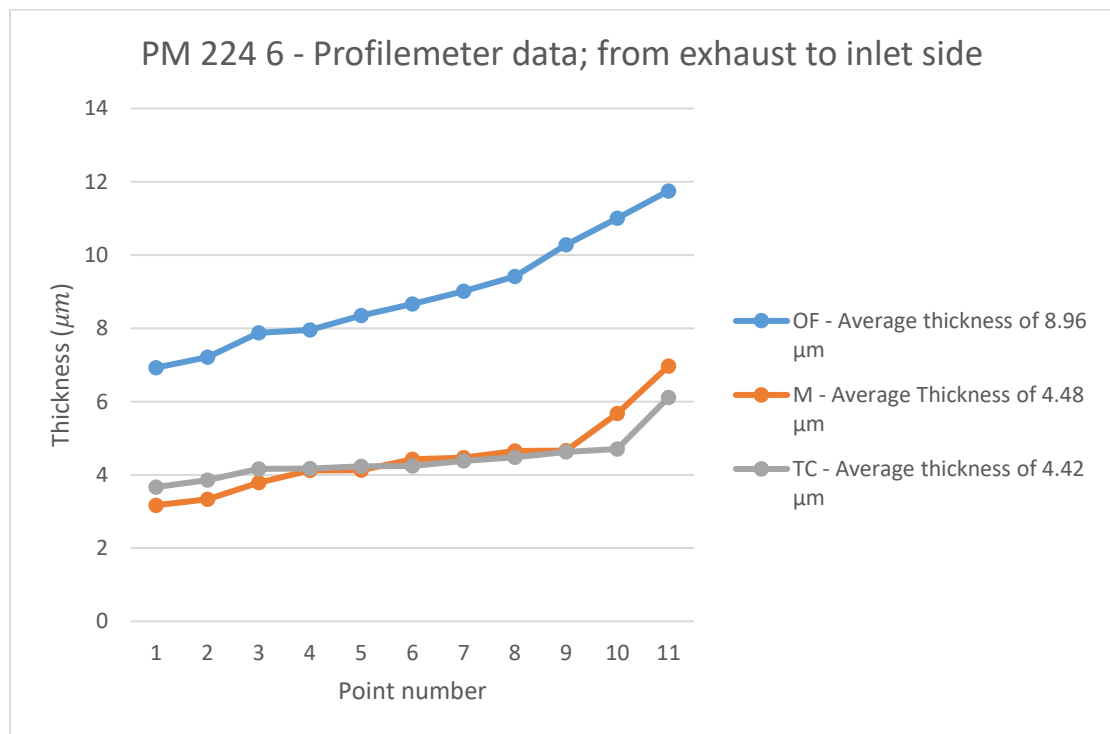


Figure 3.60 PM 224 6 – Profilometer data of samples cut in the middle (M), TC end (TC), and Out far end (OF). Middle(M) refers to sample cut exactly in the middle of the tape length.

From Figure 3.60, it is clearly seen that the thickness of the REBCO film near the Out Far end is nearly twice that of the thickness of the film deposited in the middle and the TC end. This can explain the initial spike seen in the intensity of the REBCO (005) peak (first 10 exposures in Figure 3.54). This can also partly explain the higher I_c seen towards the OF end in Figure 3.59 though the decline in seen in the I_c moving from the OF end to the TC end cannot be fully explained in terms of thickness alone since Figure 3.60 does not have data for locations between OF and Middle.

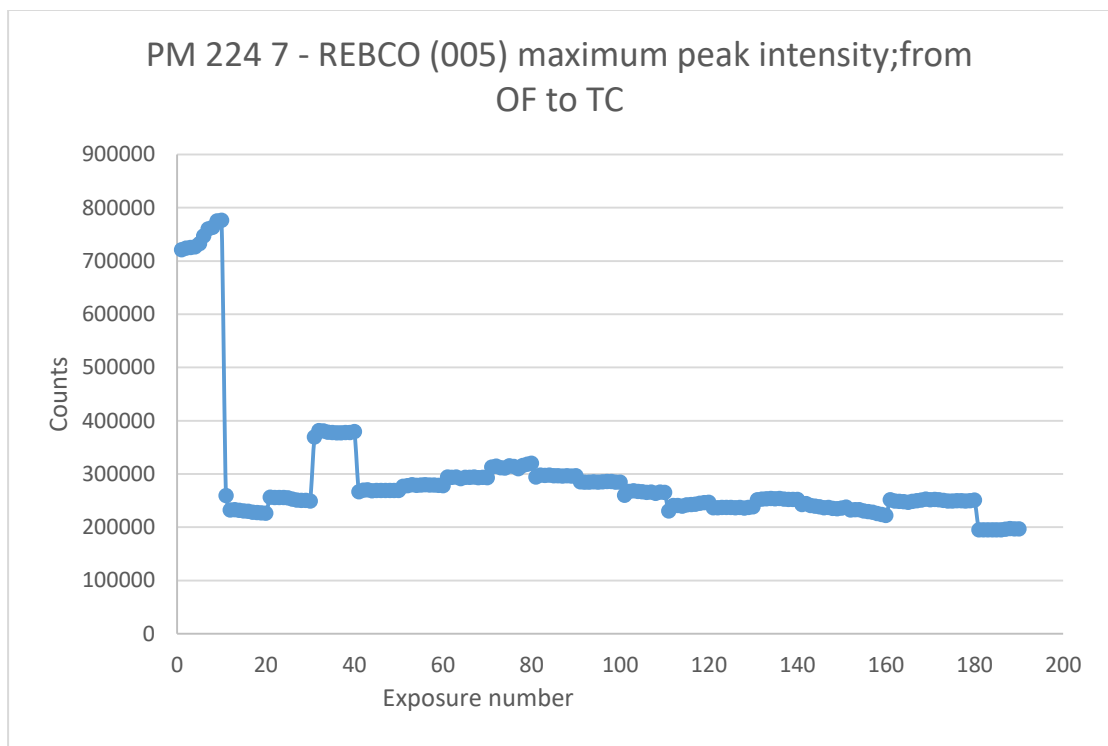


Figure 3.61 PM 224 7 – REBCO (005) maximum peak intensity vs exposure number

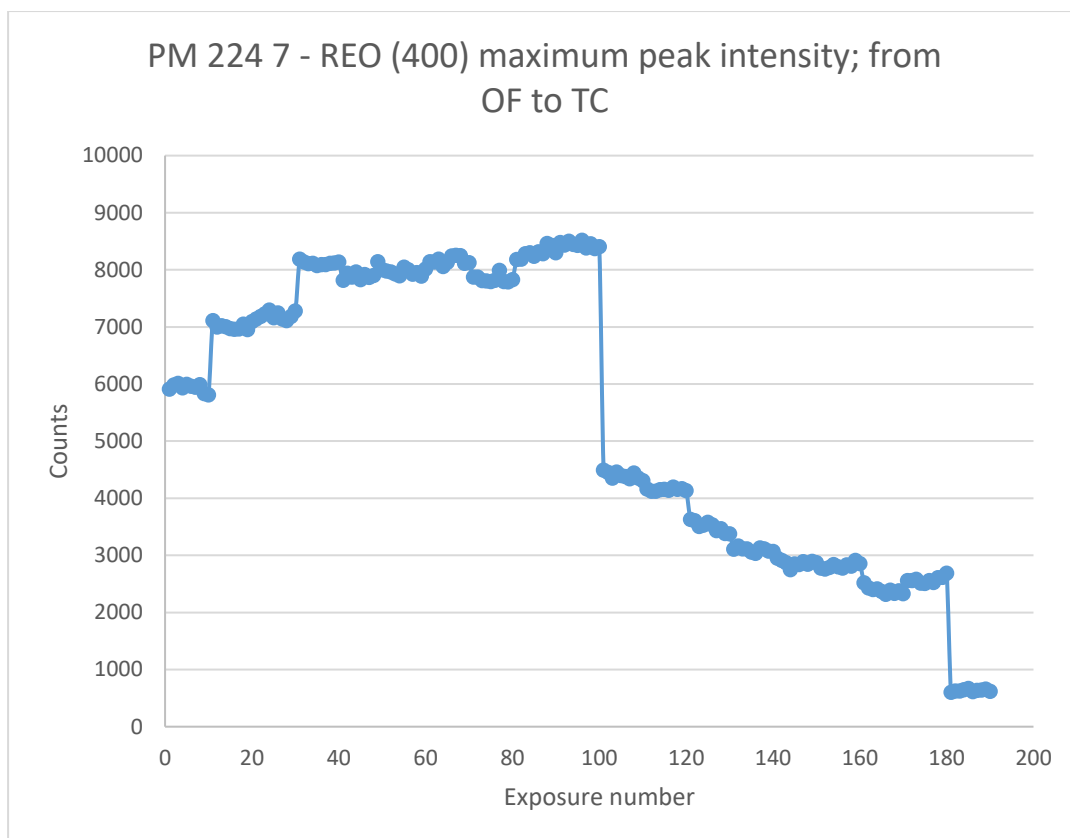


Figure 3.62 PM 224 7 – REO (400) maximum peak intensity vs exposure number

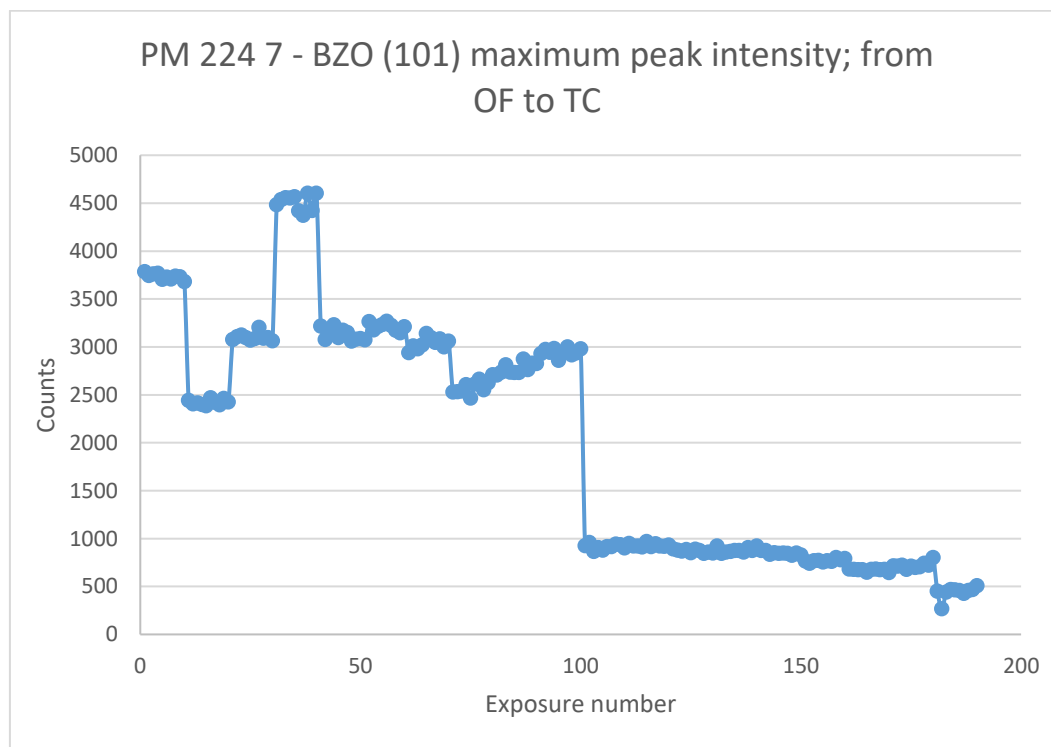


Figure 3.63 PM 224 7 – BZO (101) maximum peak intensity vs exposure number

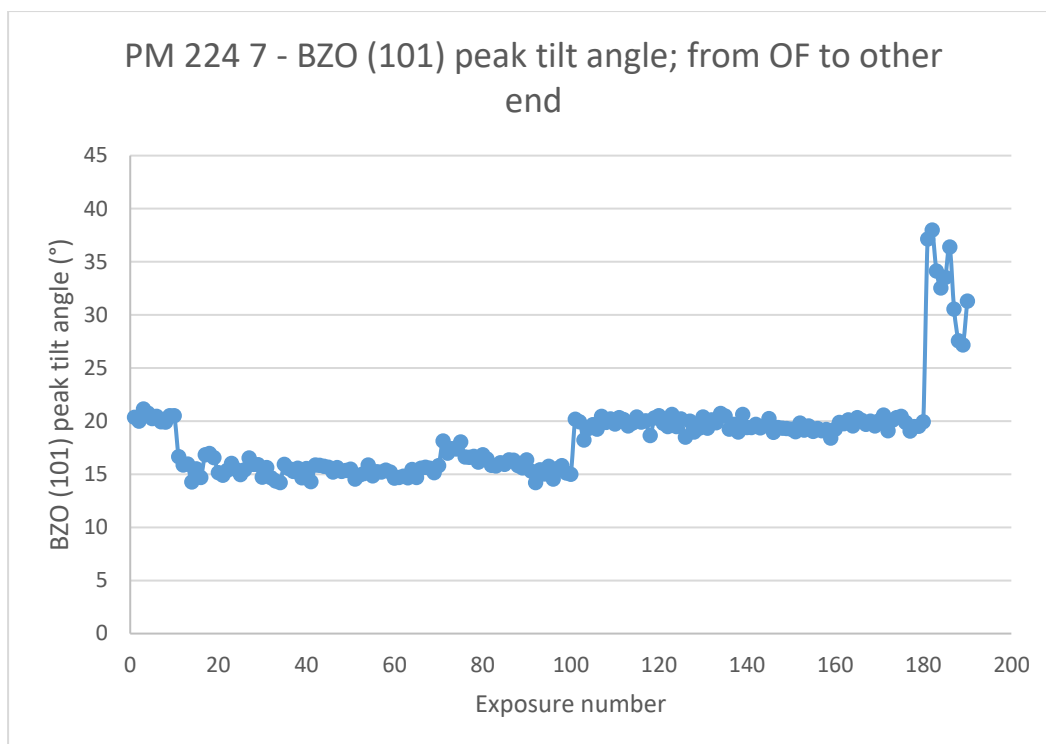


Figure 3.64 PM 224 7 – BZO (101) peak tilt angle vs exposure number

PM 224 7 shows characteristics that are similar to that of PM 224 6 with the peak tilt angle fitting with an average of 18.44 degrees and a standard deviation of 2.01 degrees (Figure 3.64). The spike in the tilt angle observed after 180 exposures is due to poor signal to noise ratio at the end of the tape and can be neglected. The average value of the tilt angle of PM 224 7 (18.48°) matches closely with that of PM 224 6 (19.89°) but the standard deviation of PM 224 7 is almost two degrees higher than that of PM 224 6 due to higher intra tape variation. A very similar pattern to that of PM 224 – 6 is seen in Figure 3.55 and Figure 3.57 with the REBCO (005) and BZO (101) peak intensities dropping in concert after ten exposures while the REO (400) peak actually increases in value as displayed in Figure 3.58. PM 224 7 exhibits more variation in the intensity of its REO (400) peak in Figure 3.62 and BZO (101) peak in Figure 3.63 with a sharp drop in the intensity of these secondary phases after hundred exposures. The angular tilt value of the BZO (101) peak also jumps up 5 degrees after hundred exposures in Figure 3.64 but stays relatively constant in its values. Comparing these graphs to Figure 3.56 and 3.57, the uniformity of secondary phase

incorporation is much better in PM 224 6 than in PM 224 7. Future studies could be conducted on studying the angular dependence of the magnetic field performance of these tapes with different REO and BZO concentrations by examining samples from different segments of tape based on its microstructural mapping. But the self-field I_c values measured at 77 K, 0 T are identical for both the tapes.

The SHPM data of PM 224 – 7 are presented in Figure 3.65. The I_c values that are obtained in this measurement match closely with the values obtained in Figure 3.59 which are to be expected from two tapes with similar compositions and processing conditions. Reproducibility of the I_c data obtained from the SHPM from two different tapes with similar characteristics on the same measurement spool also acts as a verification check to ensure that noise is not being introduced to the setup during the SHPM measurements.

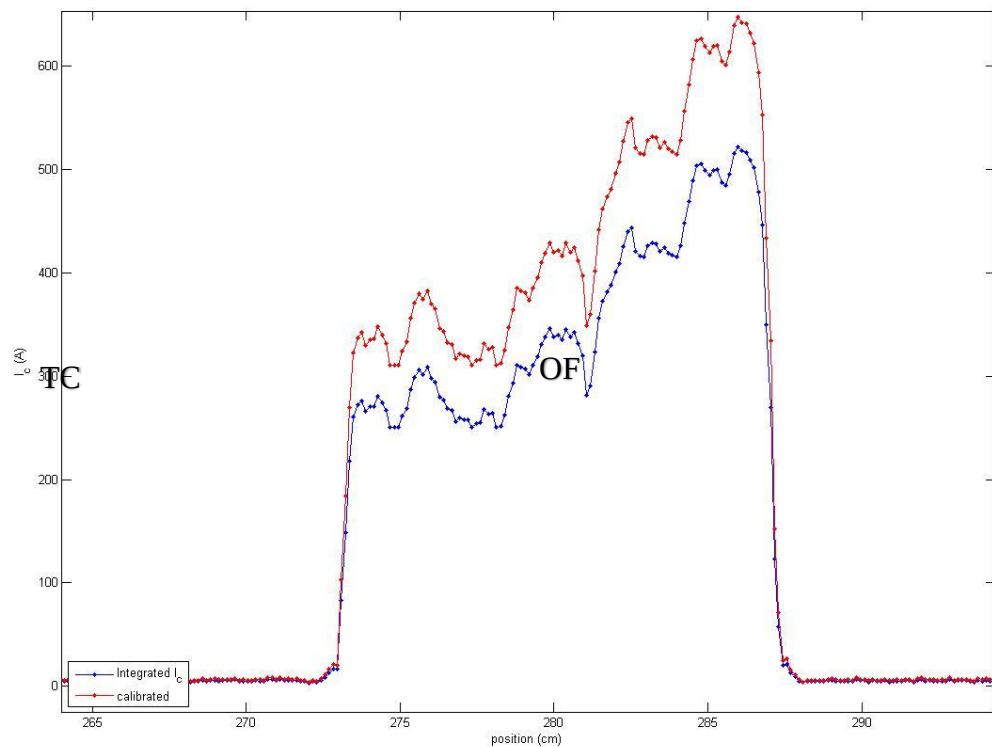


Figure 3.65 Measured I_c of PM 224 7 tape using SHPM. The OF and TC ends of the tape are marked on the graph.

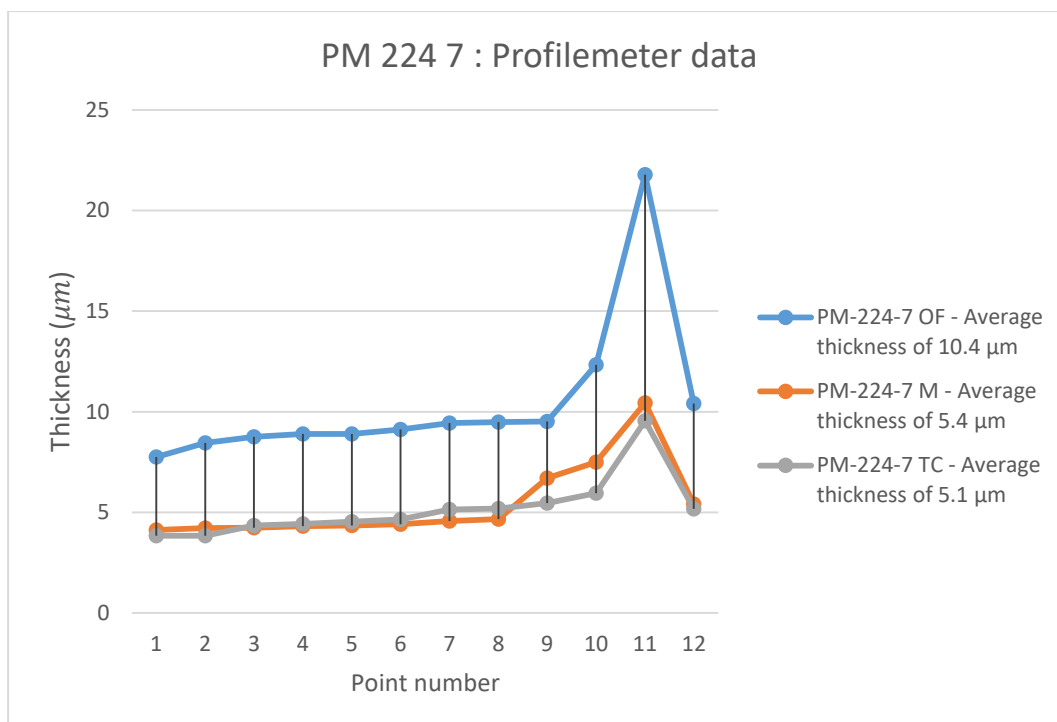


Figure 3.66 PM 224 7 - Profilometer data of samples cut in the middle (M), TC end (TC), and Out far end (OF).

Figure 3.66 shows the profilometer data of PM 224 7 tape at three different locations along the length. The thickness data obtained from Figure 3.66 shows good correlation with the REBCO (005) peak intensity data in Figure 3.61. The initial spike seen in the maximum peak count intensity correlates well with nearly double the film thickness. It should be noted that although the average film thickness is a useful metric for comparing the film thickness, the actual area of the tape from which the data are obtained will be a circle with a radius of 5.5 mm due to beam divergence, so deriving strict numerical relationships between maximum peak intensity counts and thicknesses is bound to be fraught with errors. But in the context of an inline monitoring tool capable of providing valuable real time information on film uniformity, such data will provide an immediate insight into the processing conditions for the operator which can then be used as feedback to modify the processing conditions as required. PM 224 18 and PM 224 19 were the last two tapes to be measured. These two tapes were also processed under nearly identical conditions, so similar characteristics are expected in the inline XRD and SHPM data.

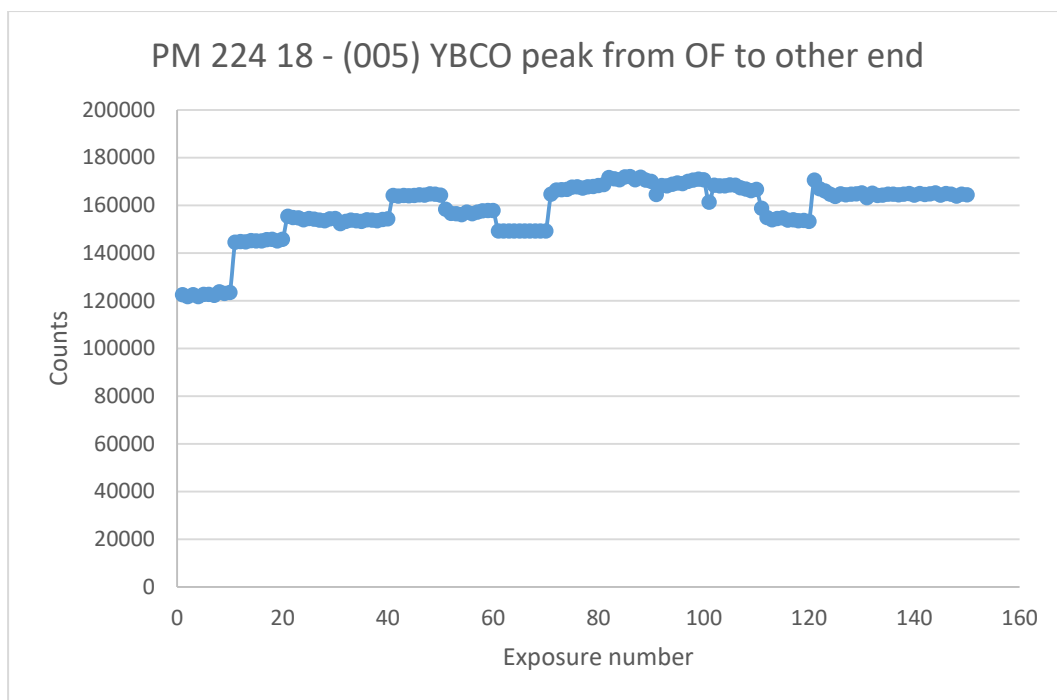


Figure 3.67 PM 224 18 – REBCO (005) maximum peak intensity vs exposure number.

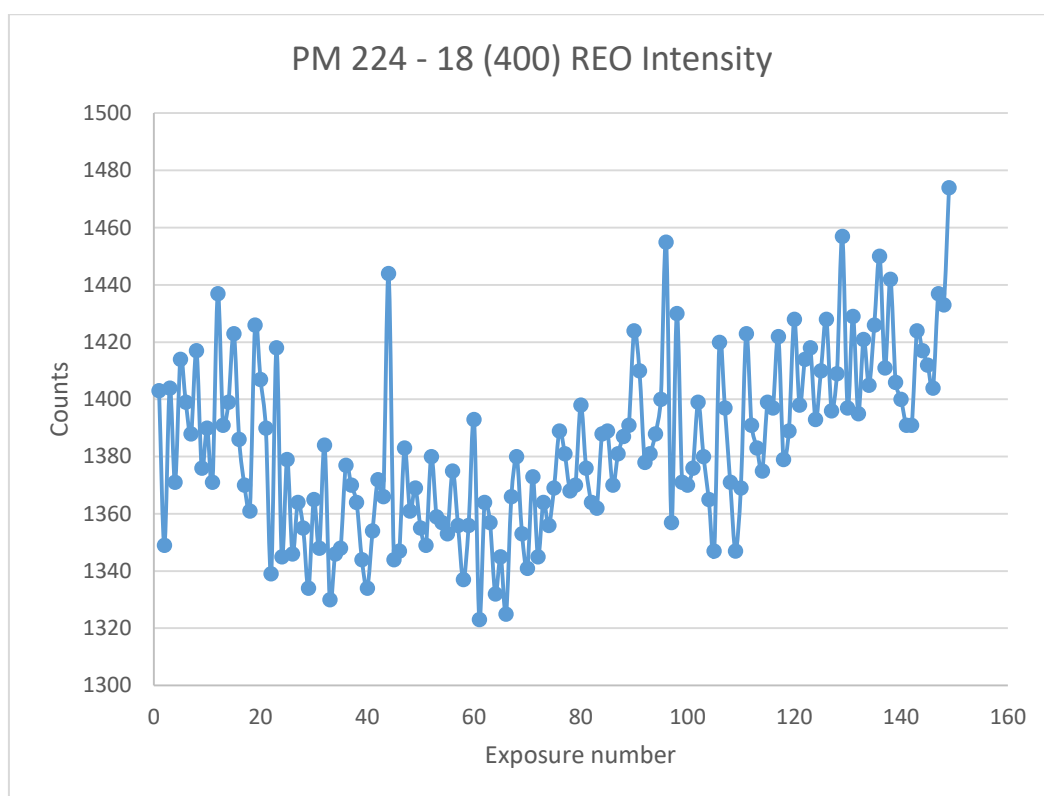


Figure 3.68 PM 224 18 – REO (400) maximum peak intensity vs exposure number.

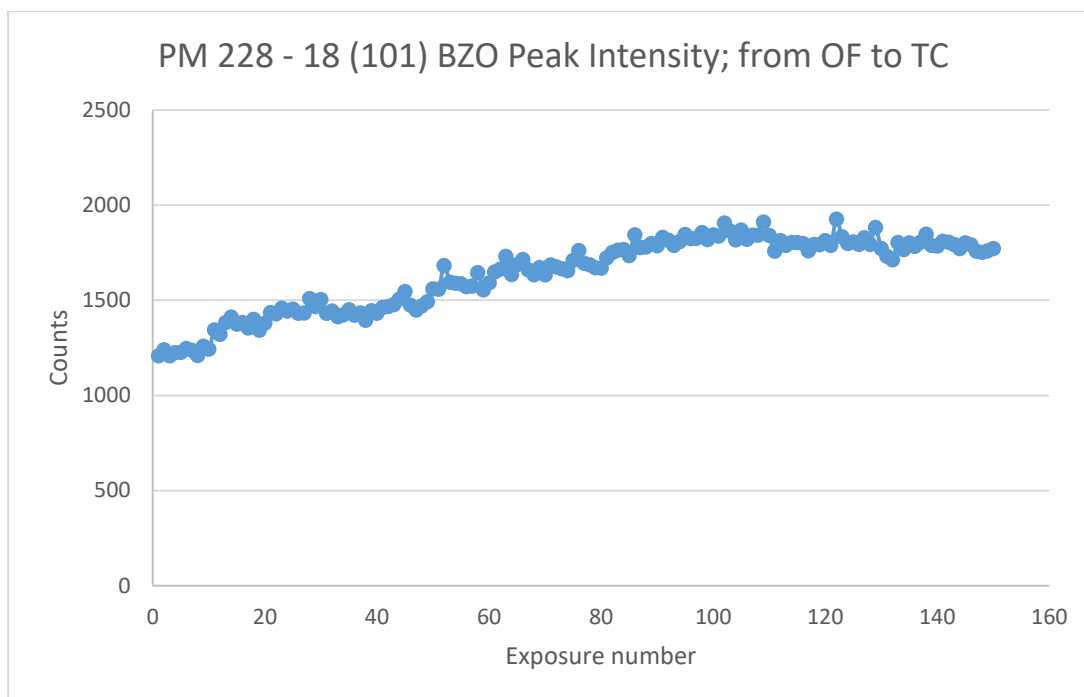


Figure 3.69 PM 224 18 – BZO (101) maximum peak intensity vs exposure number.

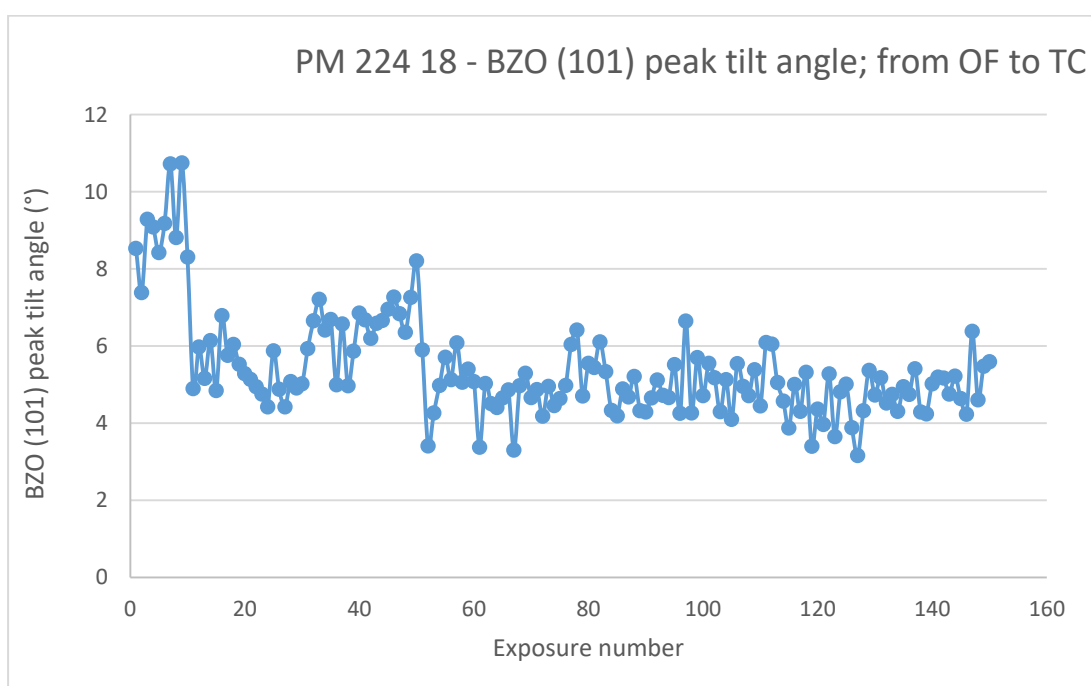


Figure 3.70 PM 224 18 – (101) BZO peak tilt angle (°) vs exposure number.

The SHPM data of PM 224 – 18 tape is shown in Figure 3.71.

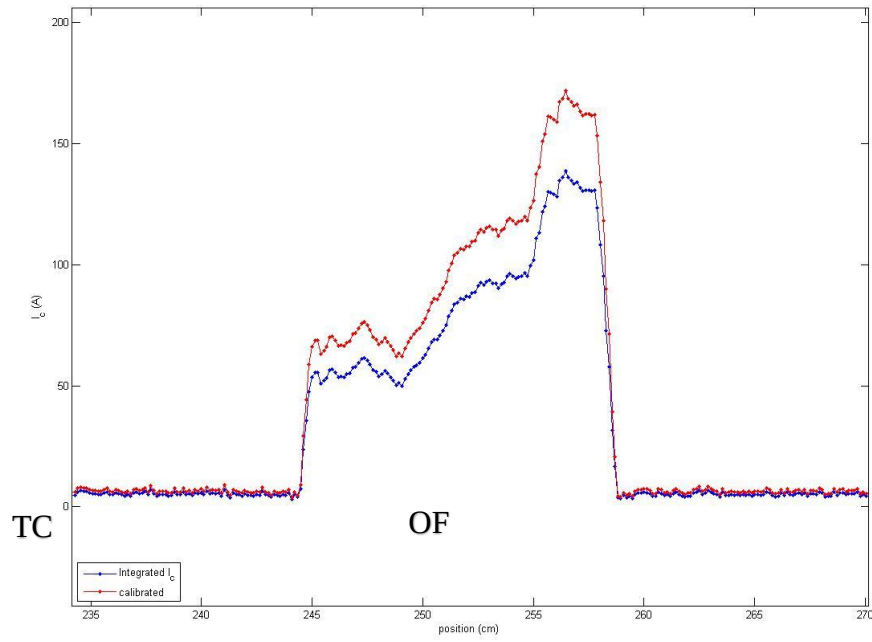


Figure 3.71 Measured I_c of PM 224 18 tape using SHPM. The OF and TC ends of the tape marked on the graph.

It is clearly seen from Figure 3.71 that PM 224 18 exhibits the same characteristic of increasing I_c towards the OF side. However, the XRD data from Figure 3.67 and the profilometer data presented in Figure 3.72 show relatively uniform thickness of REBCO deposit along the length of the tape. So this increase in I_c seen in the SHPM profile cannot be explained on the grounds of increasing film thickness.

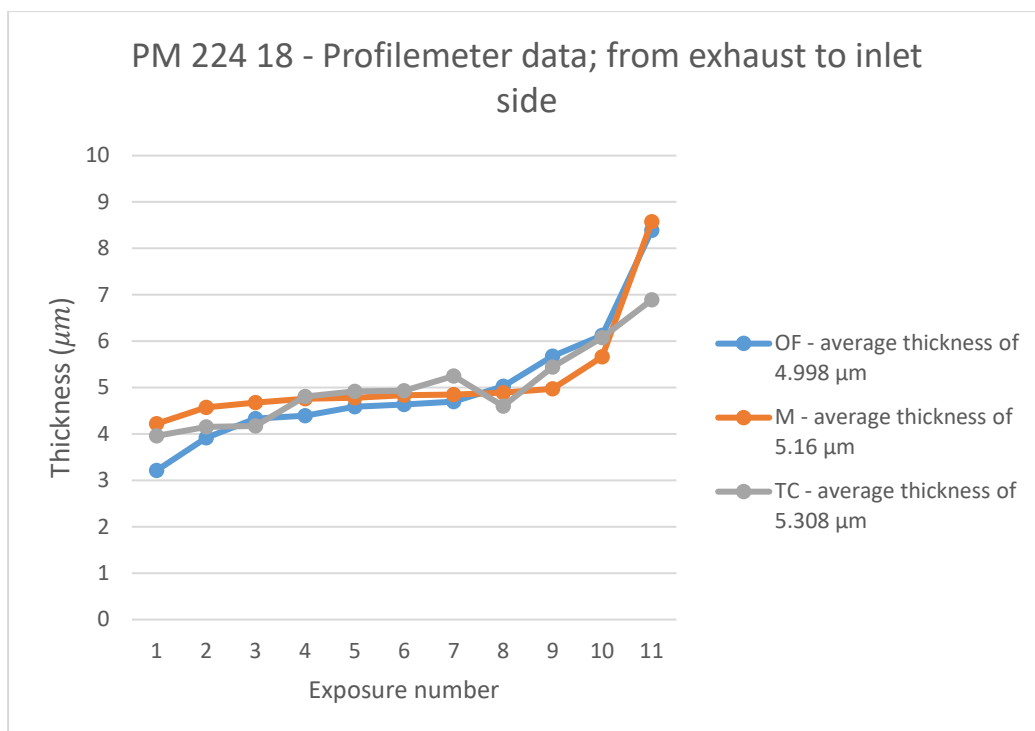


Figure 3.72 Profilometer thickness data of PM 224 18 samples cut from three different locations along tape length – Out Far (OF), Middle (M) and TC end.

The inline XRD data of PM 224 19 is shown from Figure 3.73 – 3.76.

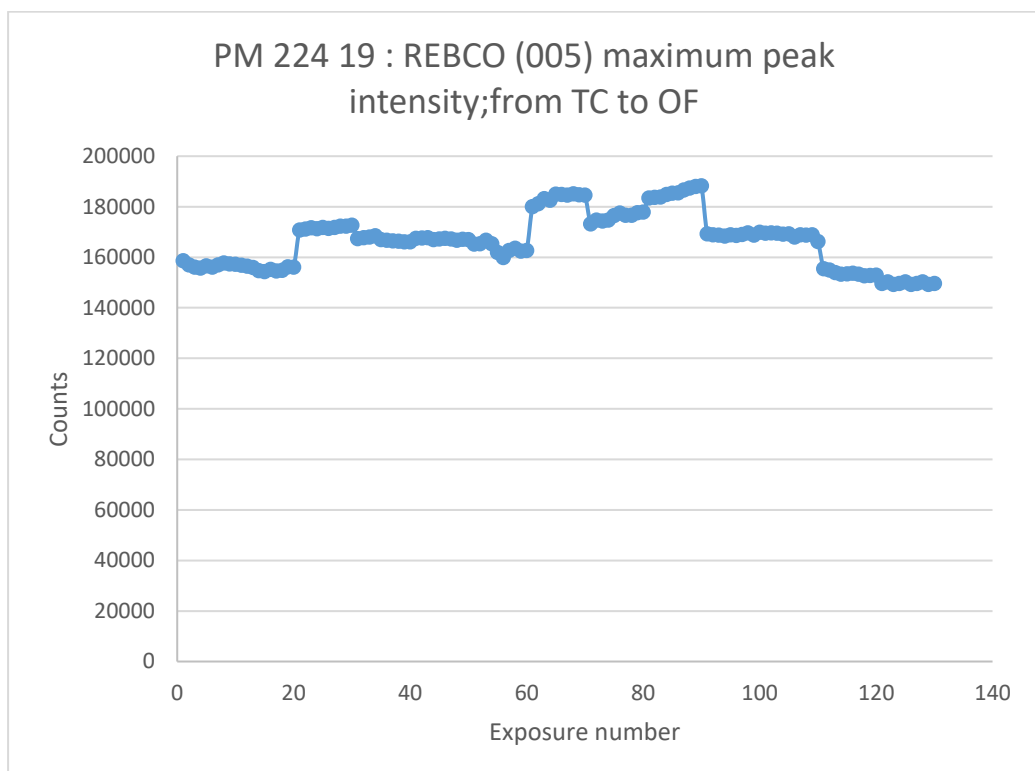


Figure 3.73 PM 224 19 – REBCO (005) maximum peak intensity vs exposure number

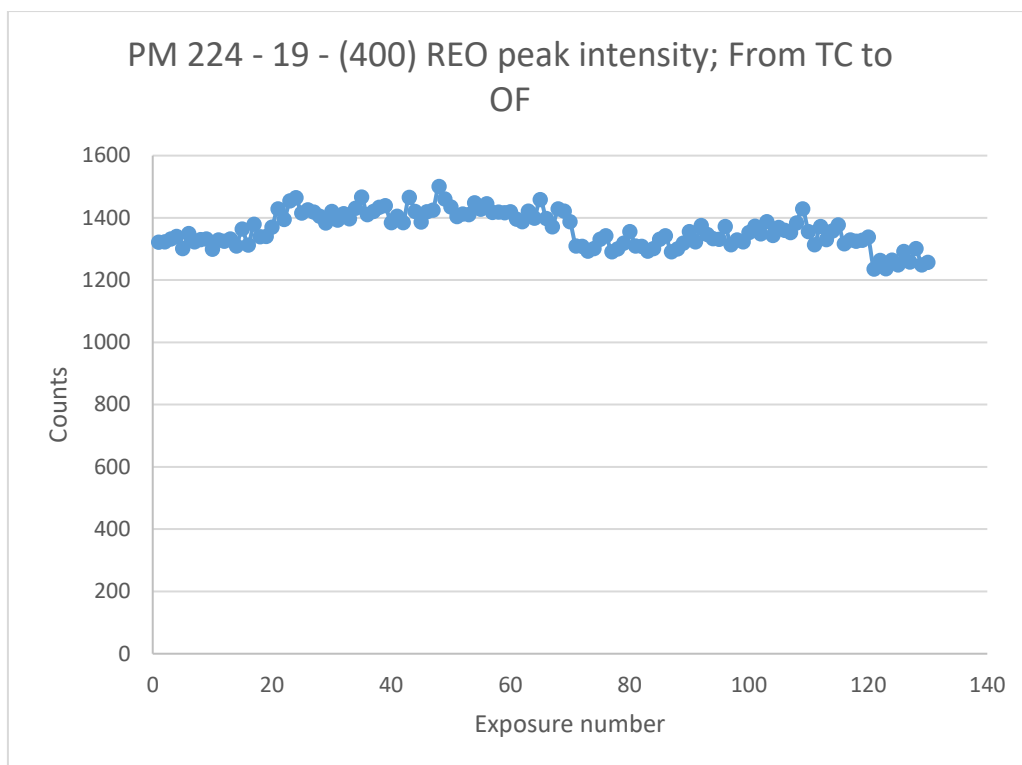


Figure 3.74 PM 224 19 - REO (400) maximum peak intensity vs exposure number

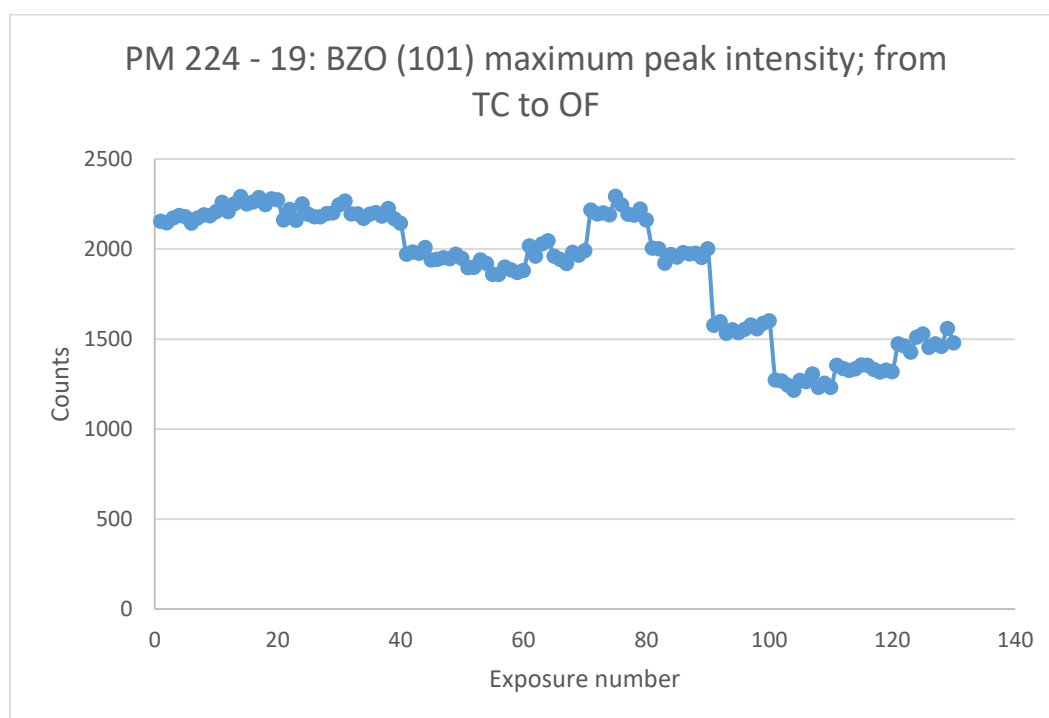


Figure 3.75 PM 224 19 - BZO (101) maximum peak intensity vs exposure number

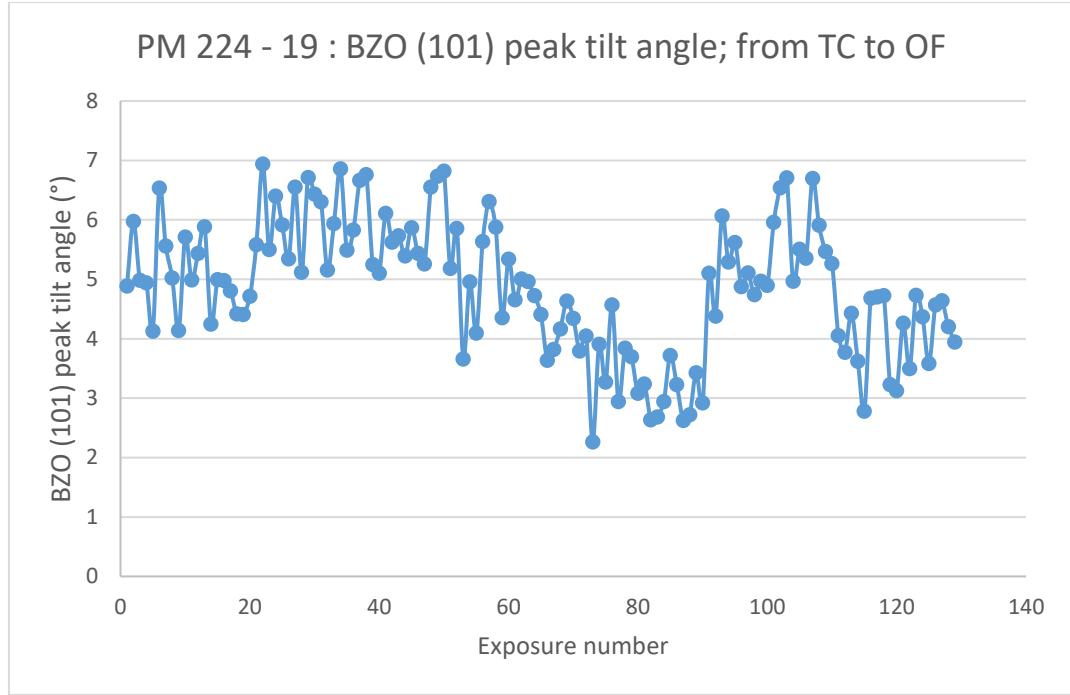


Figure 3.76 PM 224 19 – BZO (101) peak tilt angle vs exposure number

Both PM 224 – 19 and PM 224 – 18 which were processed under nearly identical conditions show similar characteristics; PM 224 18 has an average peak tilt angular value of 5.42 degrees with a variance of 1.32 degrees while PM 224 19 has an average peak tilt angular value of 4.86 degrees with a variance of 1.23 degrees. The proximity of these statistical values between two tapes of nearly similar composition and microstructure is a good indicator of the replicability and reproducibility of the inline XRD instrument. The incorporation of secondary phases in both the tapes is quite uniform except for the BZO (101) incorporation after ninety exposures in Figure 3.75 in PM 224 19 where it decreases. But the self-field I_c values are quite comparable to each other. These two samples again act as a verification check for both the inline XRD and SHPM data.

Figure 3.77 shows the SHPM data obtained for PM 224 19. The pattern seen in the SHPM measurement is very similar to PM 224 18 in that there is a maximum towards the OF end and a decaying tail towards the TC end. This pattern is observed on almost all PM tapes studied in this work and increasing thickness towards the OF end can partially explain the higher I_c starting at that end but the monotonic decay towards the TC side cannot be explained

on grounds of thickness alone. Figure 3.78 shows a slightly higher average thickness towards the OF end although the XRD REBCO (005) maximum peak intensity data from Figure 3.73 show relatively uniform maximum peak intensity throughout the length of the tape. This might be attributed to the fact that the profilometer sample was measured close to the tape end as opposed to the XRD whose measurements begin about 1 cm away from the ends to obtain a good signal-to-noise ratio since the tape microstructure begins to degrade quite severely close to the edge. So it is possible that the profilometer OF tape section lies outside the regime of the XRD measurements.

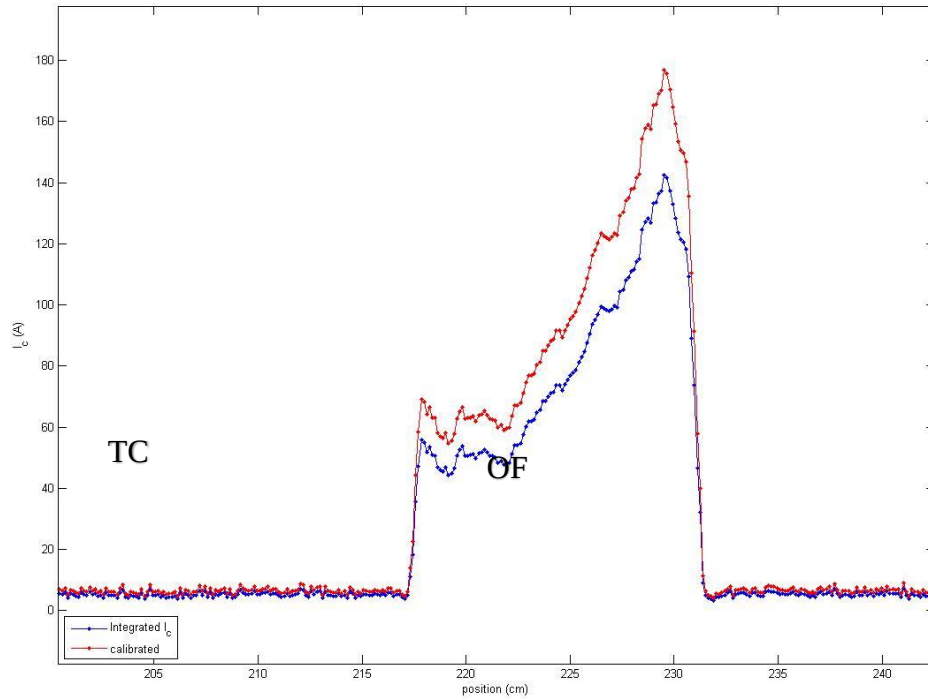


Figure 3.77 Measured I_c of PM 224 19 tape using SHPM. The OF and TC ends of the tape are marked on the graph.

Figure 3.78 shows the variation in the thickness profile of the PM 224 19 samples cut at three different locations.

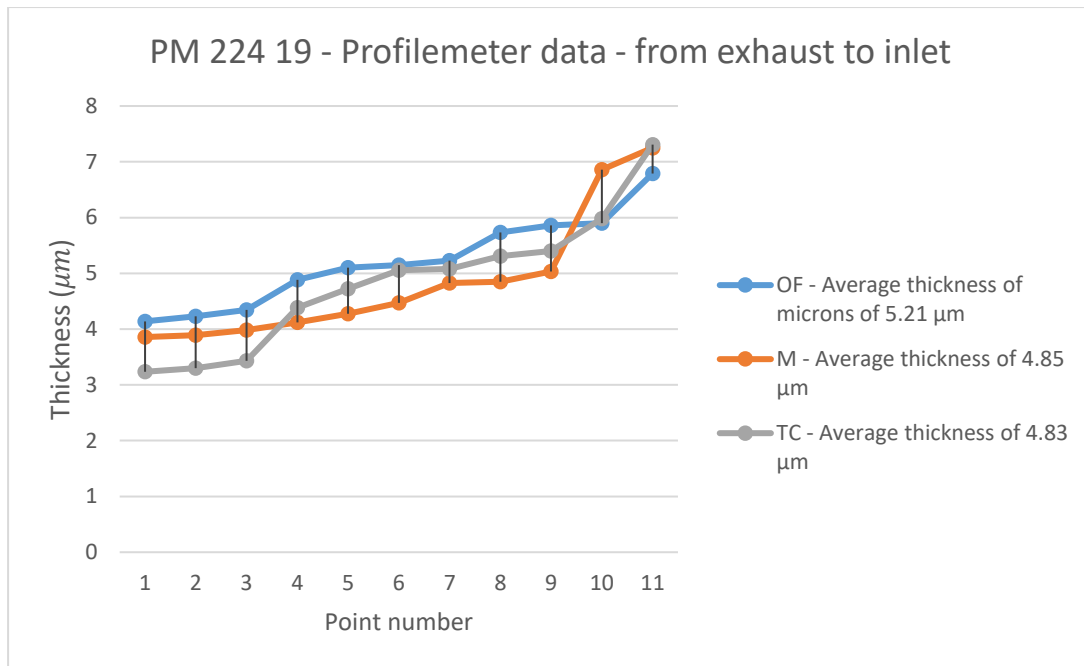


Figure 3.78 Profilometer thickness data of PM 224 19 samples cut from three different sections– Out Far (OF), Middle (M) and TC end.

Plotting all the BZO (101) peak tilt data together from the microstructural mapping of all the tapes described in Table 3.2, it can clearly be seen that despite the noise introduced by the algorithm inducing some variance in the measurements, the tapes are distinguishable from each other by virtue of their tilt angles. Table 3.5 lists out the statistics involved in each measurement. The tapes are unequal in length so the length of some of the measurements is shorter than others. However not all of the variation that is seen between tapes or within a tape is due to noise. PPMS measurements will be explored in the next section which correlates these parameters to magnetic field performance and ICP MS compositional information.

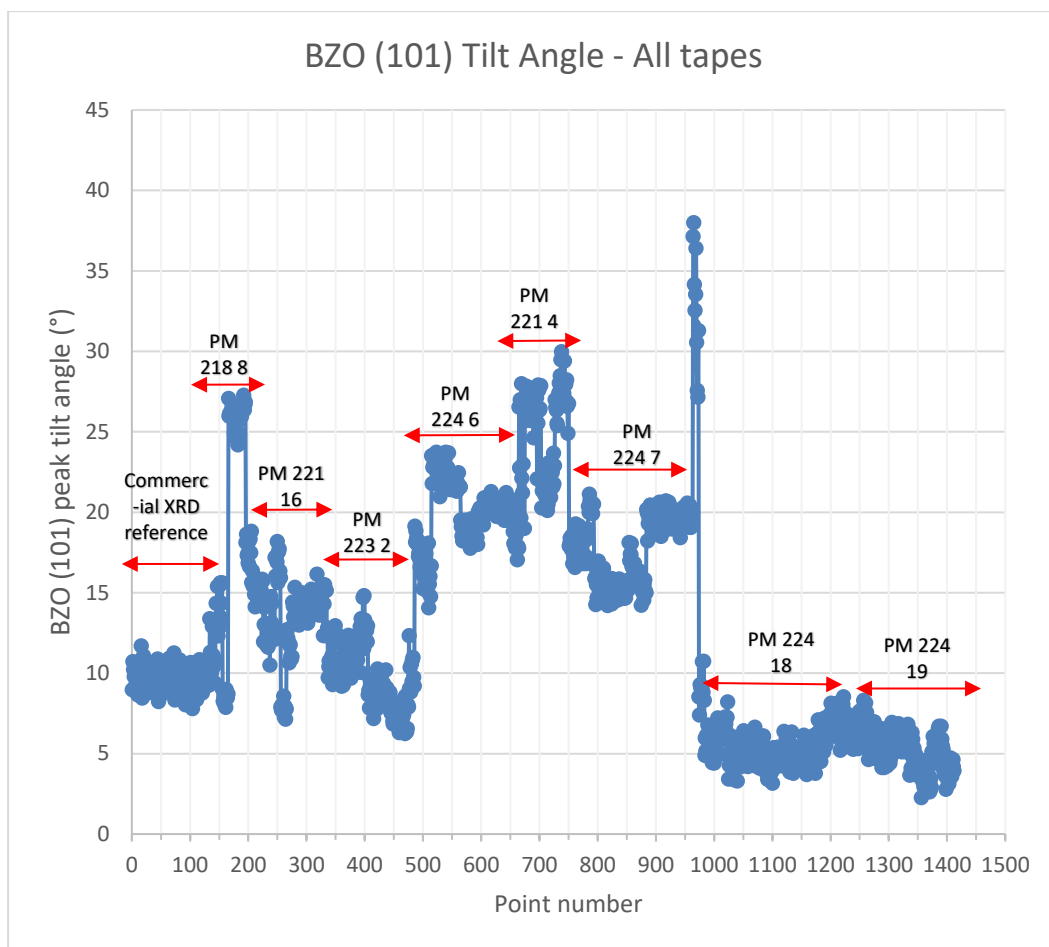


Figure 3.79 BZO (101) peak tilt angle (°) of all the tapes stitched together.

Table 3.5 – Statistics of all the measurements conducted using the inline 2D GADDS XRD in reel to reel mode.

Sample ID	Total number of exposures	Average tilt angle(°)	Standard deviation (°)
Commercial XRD reference	155	10.14	1.41
PM 218 8	100	21.78	3.20
PM 221 16	100	12.74	2.18
PM 223 2	130	9.64	1.85
PM 224 6	180	19.89	2.03
PM 221 4	120	23.12	3.96
PM 224 7	190	18.48	4.08
PM 224 18	150	5.42	1.32
PM 224 19	130	4.86	1.23

The intensity of a peak diffracted by a set of planes in a polycrystalline sample is given by [108]

$$I_{hkl} = I_0 r_e^2 \left(\frac{1 + \cos^2 2\theta}{16 \pi R \sin \theta \sin 2\theta} \right) \left(\frac{\lambda^3 n_{hkl} |F_{hkl}|^2}{V_C^2} \right) dV, \quad (3.10)$$

where I_{hkl} = diffracted intensity;

I_0 = incident intensity;

r_e = radius of electron;

2θ = diffraction angle of the plane;

n_{hkl} = multiplicity of the planes under consideration;

λ = wavelength of the incident X ray;

V_c = volume of the unit cell;

$$dV = M\delta V;$$

where M = number of elementary crystals in the sample;

δV = average volume of elementary crystals;

$$|F_{hkl}|^2 = \iiint_{cell} f_{xyz} e^{2\pi i(hx+ky+lz)} dV;$$

where f_{xyz} = scattering factor of the atom located at the
crystallographic site with coordinates (x,y,z).

It is clear from Equation 3.10 that the intensity of a peak in X ray diffraction is a multivariate function that is dependent upon a number of physical and chemical parameters of the crystal. Integrated peak intensity (area under the graph of Intensity vs 2 Theta graph) is a useful parameter capable of tracking the total diffraction volume of the REBCO crystal that is participating in the diffraction measurements. It serves as a better metric of comparison than maximum peak intensity between tapes processed at different temperatures and chemical composition and accounts for grain size variation and mosaicity of the crystal structure leading to peak broadening. The average integrated peak intensity refers to the average integrated peak intensity of the REBCO (005) peak from the entire tape measured on all the points across its length. A standard error of the mean is provided since each tape was of a different length and possessed unique non-uniformities so the degree of data dispersion is different in every case.

The average REBCO (005) integrated peak intensity serves as a holistic metric for the entirety of the tape as opposed to measuring at discrete points. This metric can therefore be used to gauge the quality of an entire tape and compared to a reference tape to check for both physical and chemical homogeneity.

Even though the film in the commercial M4 reference tape is only 1.5 μm thick, it is found to have a slightly higher integrated REBCO (005) peak intensity than most PM tapes in Figure 3.80. Assuming that the average grain size does not vary by much from the commercial tape to the thick films grown by AMOCVD, the number of crystals involved in

the diffraction pattern of the PM tapes should be three times higher. But both PM 224 7 and PM 224 6 stand out in the sense of having a higher average integrated peak intensity than the M4 tape at a higher value of (Ba+Zr)/Cu. It can be inferred from this trend that the chemical composition of the tape plays a huge role in determining the final output intensity of the X rays diffracted by the REBCO (005) peak and more data needs to be collected to check the usefulness of this relationship.

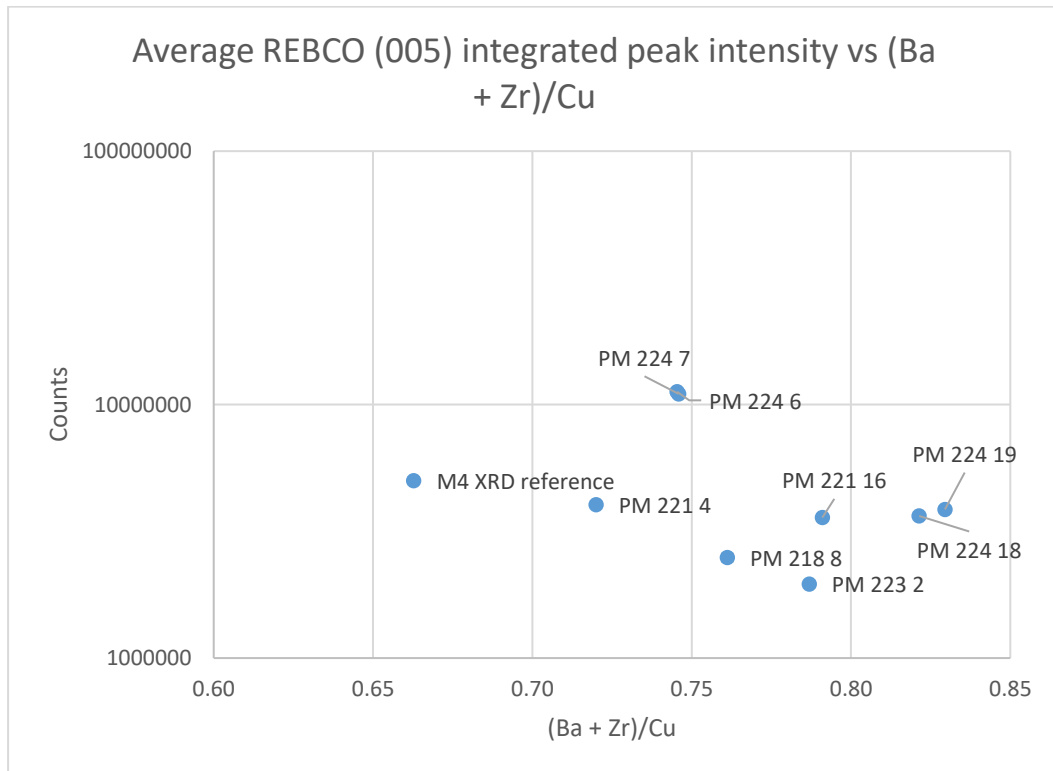


Figure 3.80 Average REBCO (005) integrated peak intensity vs (Ba+Zr)/Cu

A trend can be seen for the average self-field I_c as measured by SHPM for the entire length of the tape at 77 K , 0 T and plotted against the average integrated peak intensity of the REBCO (005) peak from the entire tape obtained from the inline XRD. This is a useful metric that can only be obtained by comparing heuristics at the level of entire tape length and not discrete point to point correlations. This is still a fuzzy correlation with PM 221 4 tape as an outlier with relative lower counts and higher I_c than the remaining tapes in Figure 3.81, but with more statistics, it can be investigated in whether an useful correlation exists. The chemical compositional dependence of self-field I_c was clearly highlighted in Figure 3.49 and

equation 3.10 discusses the effect of chemical composition of the unit cell modulating the final output intensity of the peak. So seeking a direct relationship between count intensity and self-field I_c is bound to be complicated considering the myriad set of parameters at play.

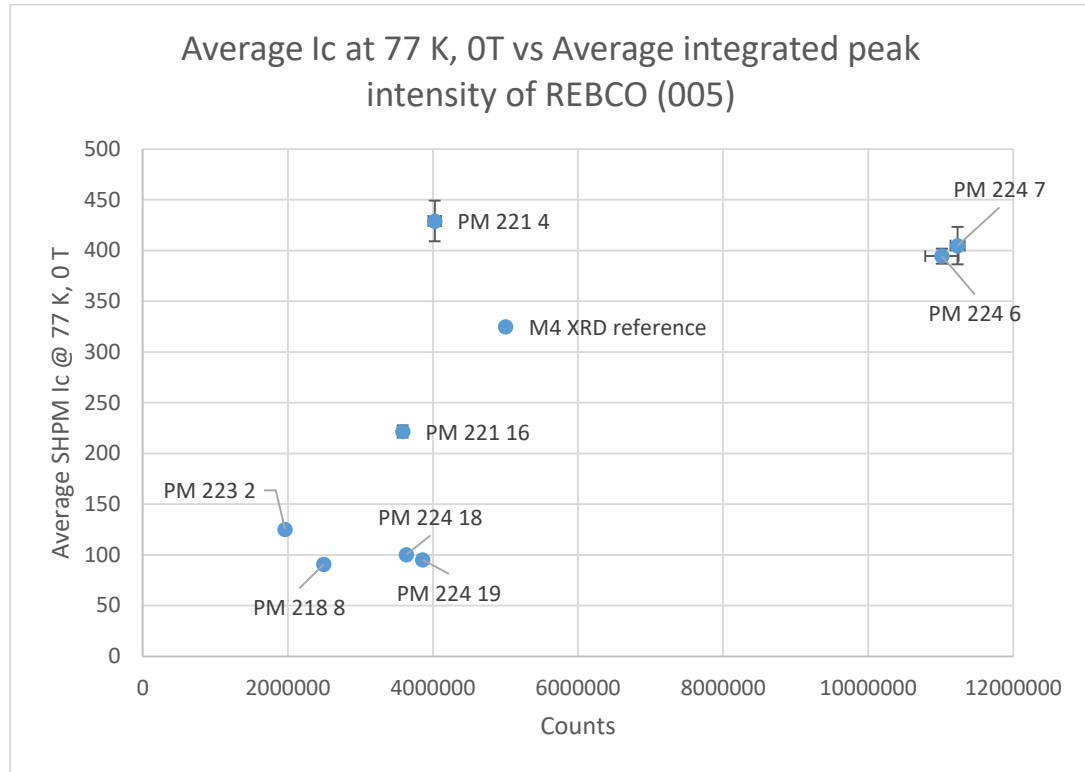


Figure 3.81 Average I_c @ 77 K, 0 T vs Average integrated peak intensity of REBCO (005).

3.1.3. Correlation of inline 2D GADDs XRD measurements with PPMS in field magnetic performance data.

After mapping out all the samples using the inline 2D GADDs XRD along the length, samples for PPMS measurements were cut roughly halfway across the length of the samples and used for in-field magnetic critical current measurements. The same samples were attached to a microscope glass slide by using an adhesive and then measured using the inline XRD. The samples were then removed from the slide and digested in 2 percent nitric acid for ICP MS analysis.

Ten exposures were collected per sample in the 2D GADDs XRD with an exposure time of 90 seconds with a 1mm slit. It can be seen from Figure 3.82 that there is substantial

amount of dispersion in the data of the BZO (101) streaking angle even when repeated at the same spot on a single tape over 10 exposures. Negative values are seen for PM 224 19 sampled due to ellipse lying almost parallel to the base of the image perpendicular to the REBCO [00L] zone axis. This causes the algorithm to fit an ellipse with a negative tilt on some of the measurements. The standard deviation in these measurements is approximately 2.1 degrees due to the weaker signal from the smaller PPMS sample size (~ 4 mm x 4 mm) that is affected by the noise contributed by the automated measurement algorithm. The ten points were averaged and then plotted against the magnetic lift factor values obtained from the PPMS in Figure 3.83. A standard error of the mean was also included with the plot in the form of error bars.

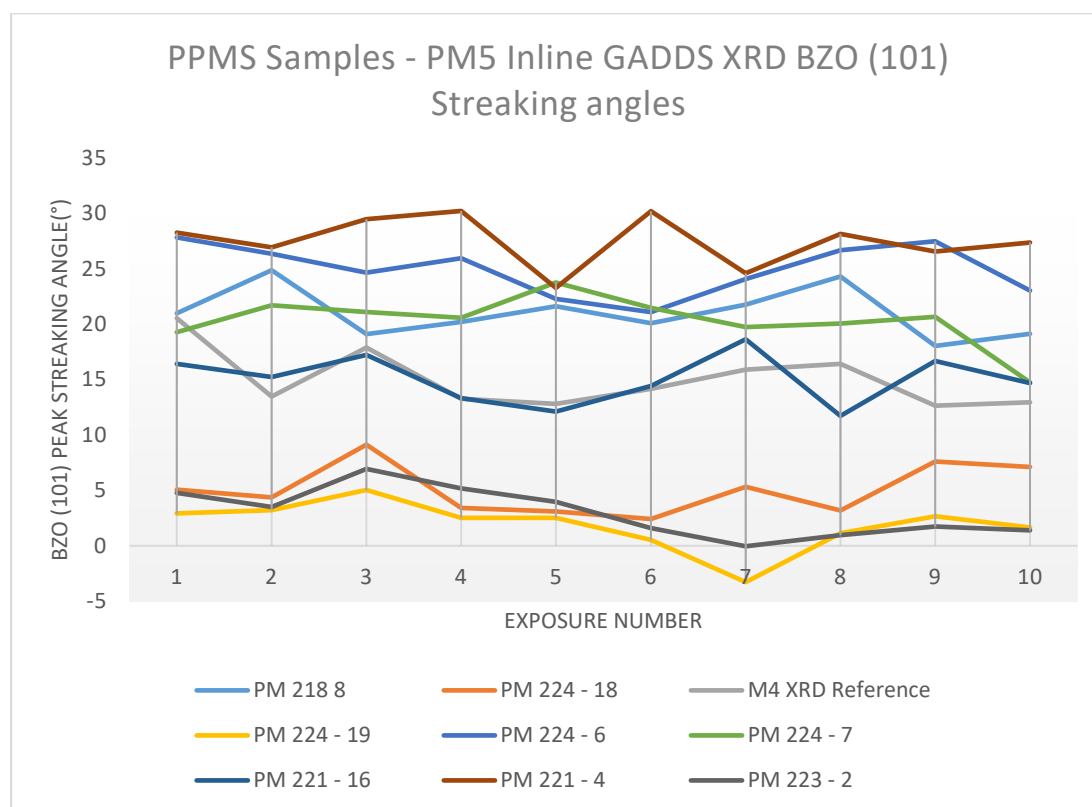


Figure 3.82 BZO (101) Peak streaking angle vs Exposure number measured on PPMS samples.

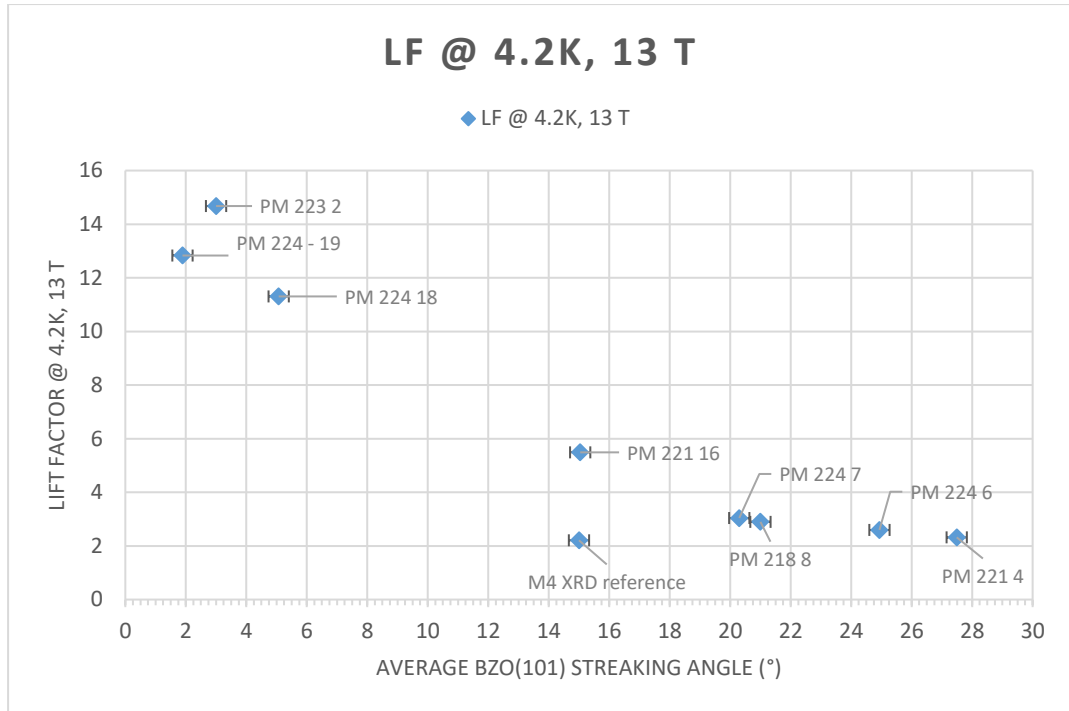


Figure 3.83 Plot of lift factor at 4.2K, 13 T vs average BZO (101) average peak streaking angle.

It is evident from Figure 3.83 that the lift factor measured using the PPMS at 4.2K, 13 T decreases as the BZO (101) average peak streaking angle increases. The one exception to the general trend seen in the AMOCVD tapes is the commercially produced M4 tape which was used as the control sample for the measurements. The thickness of the REBCO film in the M4 tape is only 1.5 μm thick as opposed to that of all the other samples from the AMOCVD which measure at least 4.5 μm . The average nanorod diameter needs to be confirmed using TEM and further studies conducted on the 1.5 μm thin film samples to understand if there is a separate trend for thinner films. It can be postulated that when the streaking angle is low, correlated c-axis pinning plays a dominant role in increasing the lift factor substantially i.e., vortex diameter matches BZO nanorod size. But at higher streaking angles beyond 20 degrees, the BZO nanorod size is so large that c-axis correlated pinning is no longer the dominant mechanism and the lift factor plateaus out. More samples need to be investigated to derive a numerical relationship between the streaking angles and lift factor.

Figure 3.84 is a graph correlating the average BZO (101) peak streaking angle with compositional variance as measured from ICP. $(\text{Ba} + \text{Zr})/\text{Cu}$ is a useful metric for measuring the BZO incorporation into the REBCO matrix and if any variation with the streaking angle can be detected, it would be a highly useful metric to track the chemical compositional homogeneity of the tape when produced in long lengths.

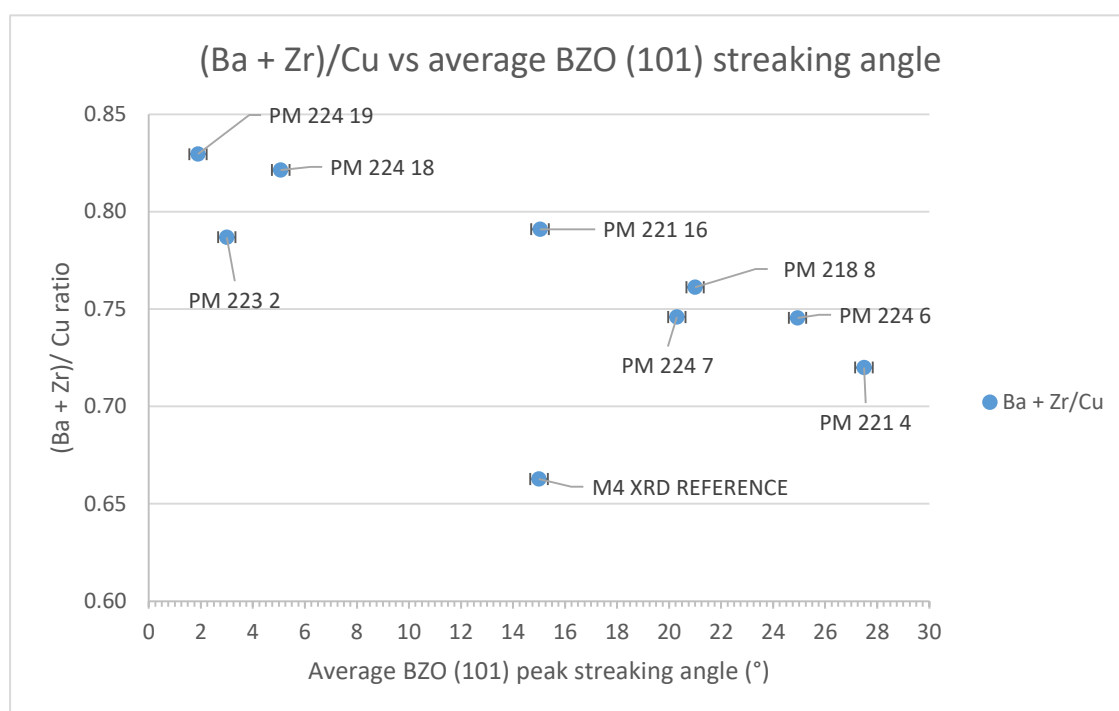


Figure 3.84 Average BZO (101) peak streaking angle vs $(\text{Ba} + \text{Zr})/\text{Cu}$ ratio.

It is clear from Figure 3.84 that despite the spread in values seen in the $(\text{Ba} + \text{Zr})/\text{Cu}$ ratios, there is a clear downward trend of decreasing streaking angle with increasing value of $(\text{Ba} + \text{Zr})/\text{Cu}$. The M4 sample again stands out from this trend due to currently unknown reasons.

Figure 3.85 displays the correlation between magnetic I_c at 4.2 K, 13 T and average BZO (101) peak streaking angle. Unfortunately, no correlations could be made on this set of tapes for this particular relationship. More tapes need to be investigated with relatively comparable self-field I_c since high barium tapes like PM 224 18 and PM 224 19 have low

self-field I_c despite the high lift factor which confounds any meaningful relationship that can be sought between magnetic I_c at 4.2 K, 13 T and average BZO (101) peak streaking angle.

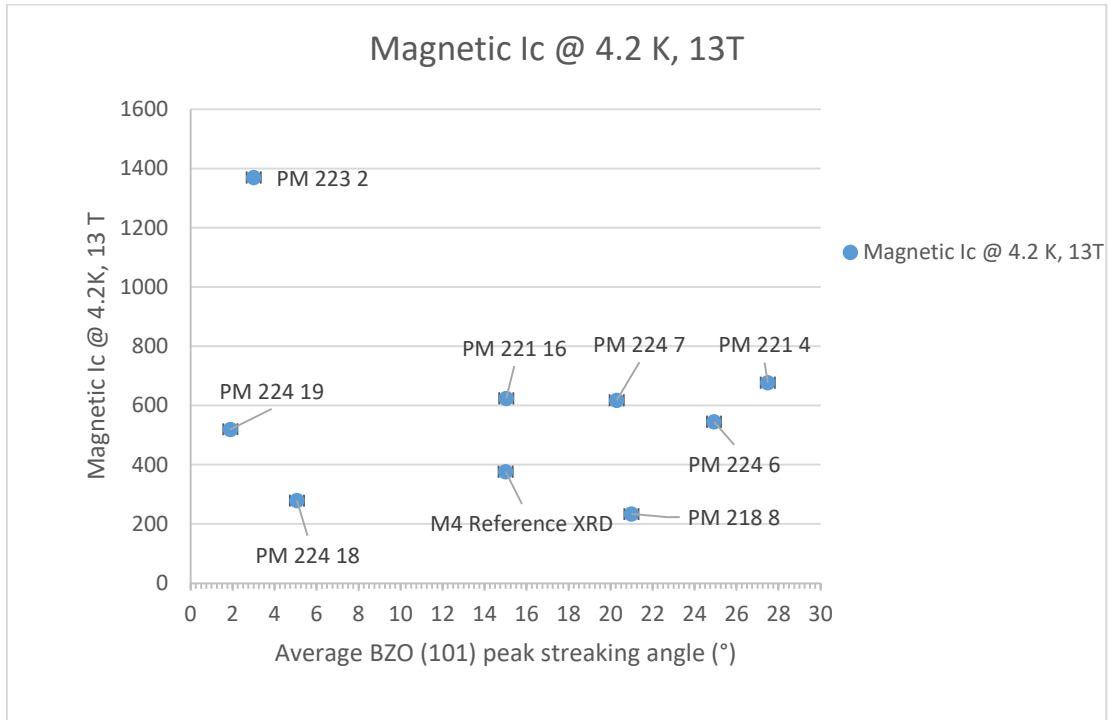


Figure 3.85 Magnetic I_c @ 4.2K, 13 T vs average BZO (101) peak streaking angle.

PM 221 4 and PM 218 8 were also cut at three different points along the length and studied using the PPMS to draw correlations with BZO (101) streaking angle data. These samples were selected since they exhibit a wide range in their BZO (101) streaking angle along the length. If intra-tape variation can be predicted as well as the inter-tape variations shown earlier, the 2D GADDS inline XRD can provide invaluable data during the actual production of long lengths of tape with homogeneous properties. Figure 3.86 is a plot displaying the streaking angles of these tapes.

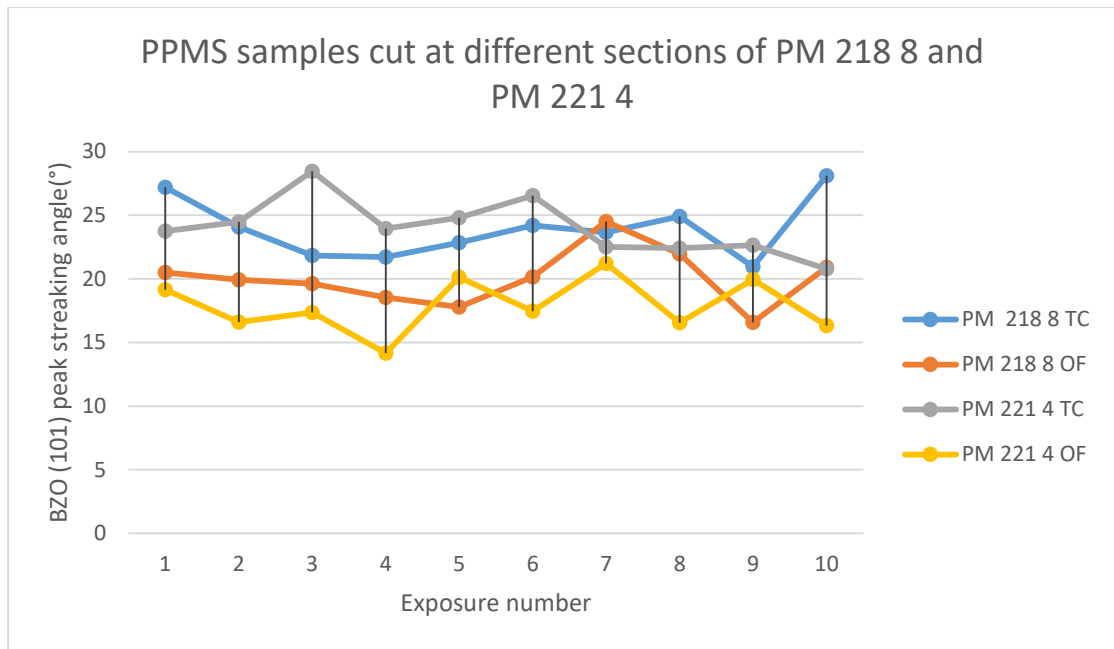


Figure 3.86 BZO (101) peak streaking angle vs exposure number for PM 218 8 and PM 221 4 cut at different sections along tape length.

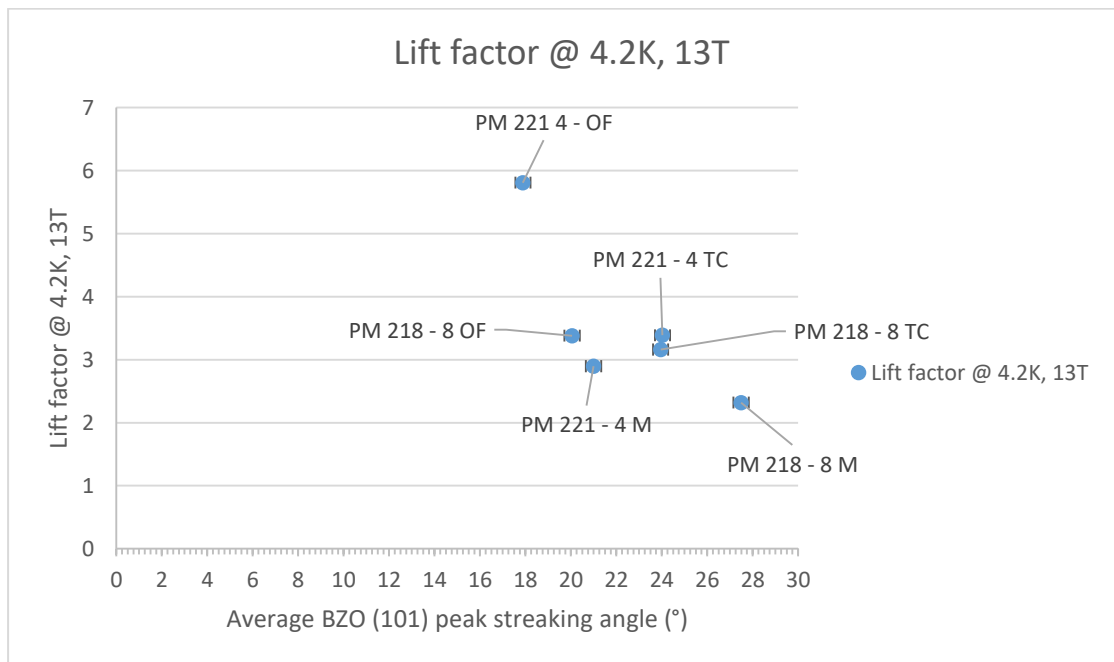


Figure 3.87 Lift factor @ 4.2K, 13 T vs average BZO (101) peak streaking angle for PM 221 - 4 and PM 218 - 8 cut at different sections on the same tape. PM 221 - 4 M and PM 218 - 8 M refer to the samples used for the previous measurements which were cut from the middle of the sample.

It can be seen from Figure 3.87 that for the PM 221- 4 OF section which seems to exhibit relatively higher lift factor, the streaking angle is substantially lower than that of 221- 4 M and PM 221-4 TC sections. A similar trend can be observed for the PM 218 samples which seem to exhibit increasing streaking angles in locations with slightly lower lift factors. But the PM 221-4 TC sample displays a slightly higher average streaking angle than PM 221- 4 M despite having a slightly lower lift factor. Variation induced by algorithmic noise also makes it hard to deduce a trend.

Figure 3.88 correlates the (Ba + Cu)/Zr ratio with the streaking angle of the six samples used above.

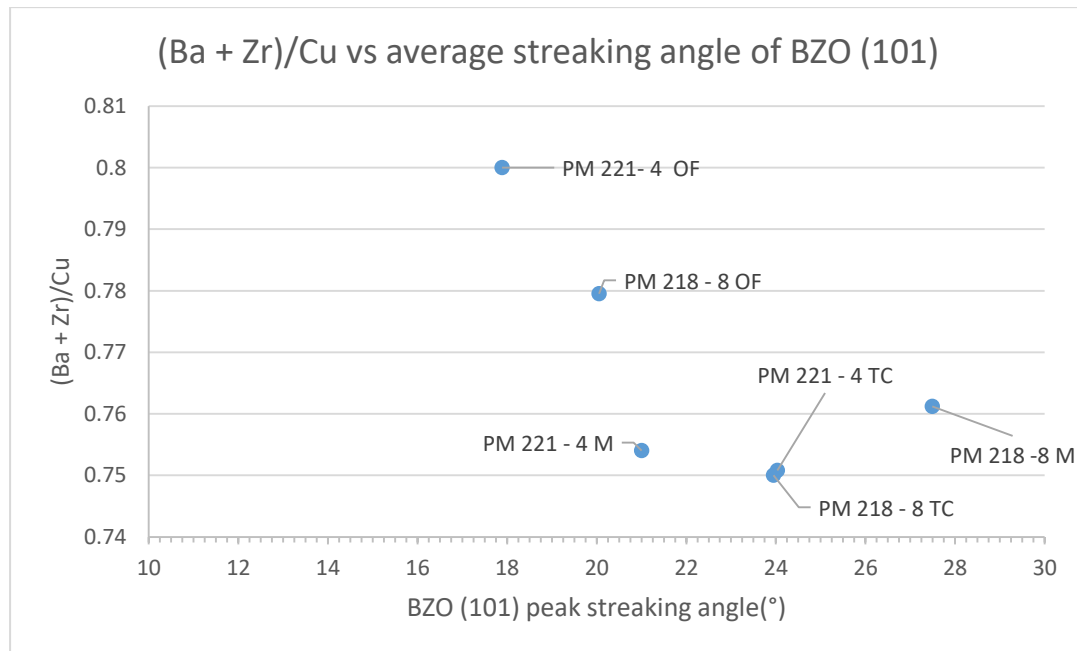


Figure 3.88 (Ba + Zr)/Cu ratio vs average streaking angle of BZO (101) for PM 221 4 and PM 218 8 cut at different sections along the length of the tape.

There is clearly an increase in the streaking angle with decreasing values of (Ba + Zr)/Cu ratios that can be observed for the PM 221 4 tape but such a trend is not being exhibited by the PM 218 8 tape in Figure 3.88. More data points need to be collected across different tapes to infer any useful trends that might be obtained from such experiments.

It can be inferred from these measurements that for samples that exhibit a streaking angle beyond 20 degrees, the nanorods have a less pronounced role in c- axis correlated pinning and the samples seem to exhibit more of a plateau behavior where the measured lift factor is no longer correlated with nanorod size. Nevertheless, substantial intra-tape variation in nanorod size and by extension, performance at 4.2K, 13 T, can be successfully tracked giving sufficient tape length and data points. Reducing noise from the automated algorithm will play a huge role in advancing this technology and improving the resolution of the instrument to discern differences due to finer variation in the structure of the nanorods and by extension, the tape's magnetic field performance.

Chapter 4

Inline measurement of precursor gas molecules using Fourier Transform Infrared Spectroscopy

4.1.1. FTIR – Setup and Experimental details

The setup has been described in detail in Chapter 2. Photos of the setup with some of the finer details will be described in the following sections.

A 4-way cross with custom feedthrough was designed to act as a flow cell. Figure 4.1 is a CAD rendering of the setup.

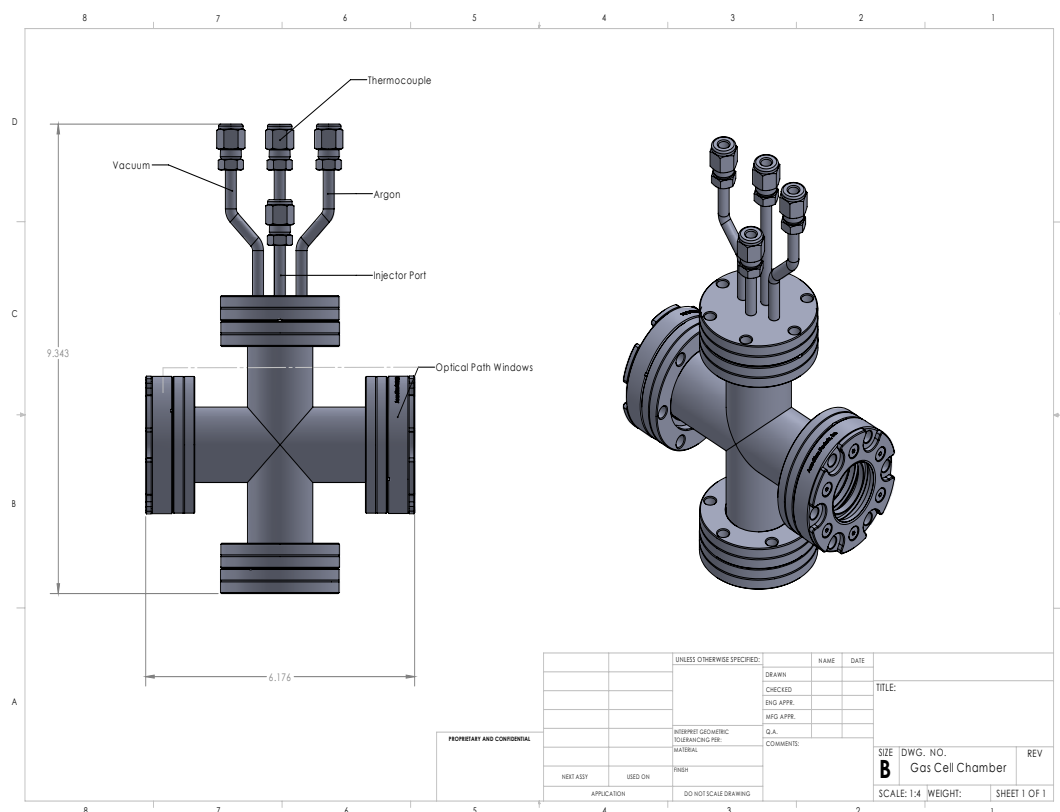


Figure 4.1 CAD drawing of gas cell with custom feedthrough.

The custom feedthrough in Figure 4.1 was fabricated by a third party vendor. Initially the setup was designed to act as a stand-alone vaporizer as well as gas cell analyzer, but, due to limitations in space and heating capacity, the setup was used as a gas cell analyzer only

with the pilot MOCVD evaporators acting as vapor sources to the setup as explained in Chapter 2. The port labelled vacuum is actually the entry port for the vapors from Evap 1. The port labelled Thermocouple was used with a Swagelok compression ferrule fitting to accommodate a K type thermocouple. This thermocouple which was suspended in midair inside the setup, acts as the vapor guide temperature monitor for the gases passing through the cell. This was also assigned as the controlling thermocouple to a PID controller which was driving a heater tape that was strategically wound around the entire cell to ensure uniform heating of the cross sections.

A number of thermocouples were placed at all the critical junction points around the setup as can be seen from Figure 4.2 which is a picture of the setup as it was being built and installed.



Figure 4.2 Photograph of the FTIR gas cell.

Potassium bromide (KBr) windows were purchased and installed on special CF optical flanges with options for custom windows from ThorLab Optics with Kalrez O-rings for high temperature operation.

Precursor residue coating on the window is a major issue that will completely prevent any meaningful analysis from being conducted. Despite heating the entire setup and ensuring adequate window temperature (KBr can withstand up to 300 °C), condensation of the vapors on the inside of the optical window was observed within half an hour of precursor flow. A special gas curtain comprising of pipes with holes drilled in them and a Swagelok Tee Union with an argon inlet pipe was inserted through the port labelled Argon. This provides a positive pressure gas stream directly at the site of the windows preventing (or at least delaying) the process of coating of precursor residues on the window. Figure 4.3 is a photograph of the setup with the gas curtain circuit installed.

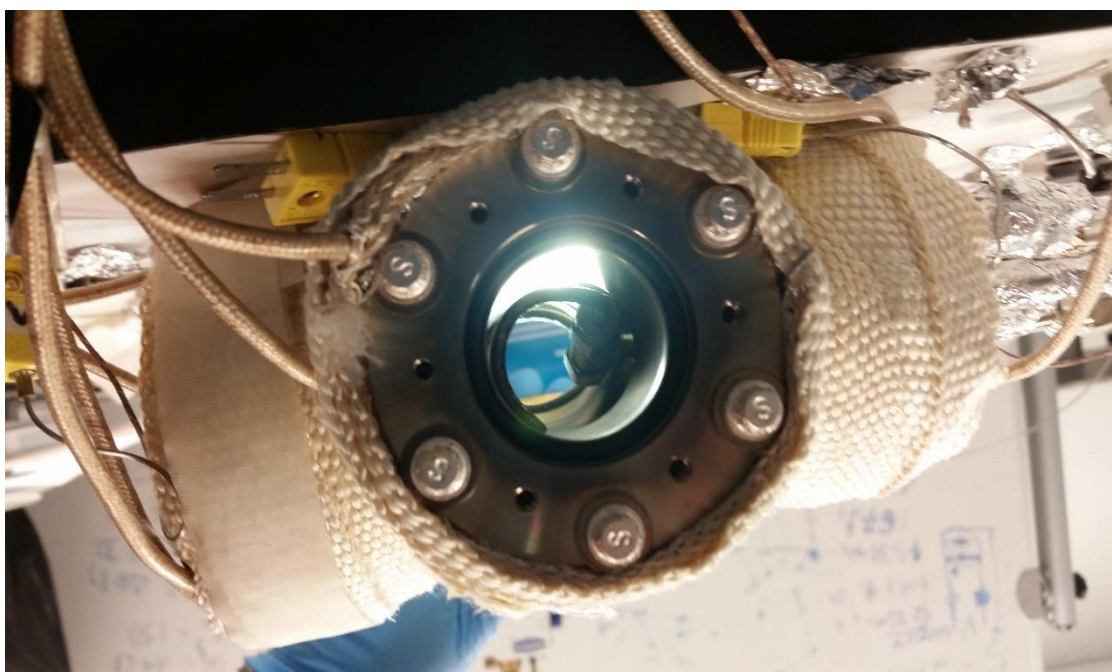


Figure 4.3 FTIR gas cell with custom gas curtain circuit coil to purge the windows. The Swagelok Union Tee is clearly visible in this photo.

After installing this circuit, the duration of the experiment could be extended to two hours without any coating hindering the measurements.

Snapshots of the entire setup is shown in Figure 4.4. A custom-Teflon-covered metal plate is installed on both the incident beam lens and detector lens on either side of the setup (the incident beam side plate is clearly visible in Figure 4.4) in order to protect the lens when the setup is hot and in standby mode between measurements.

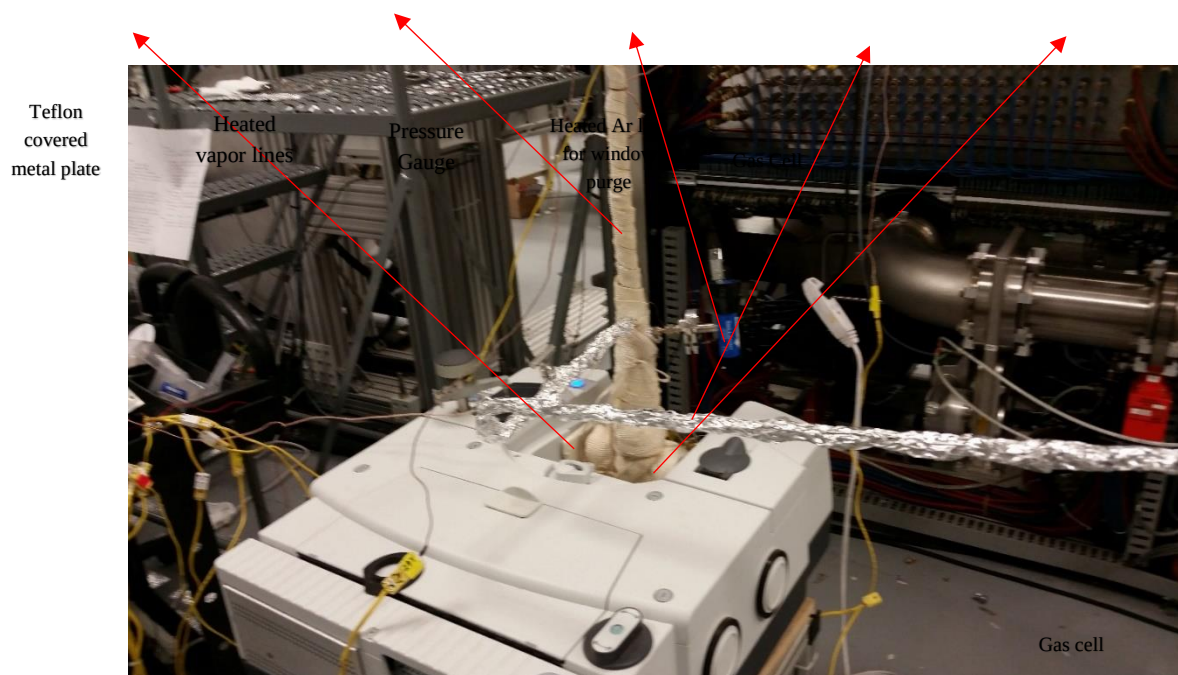


Figure 4.4 Photograph of the entire FTIR setup.

The first spectrum to be collected was that of Tetrahydrofuran (THF) which is used as the solvent for all REBCO MOCVD precursors. This spectrum will be the primary background spectrum that is to be subtracted from all the other precursor spectra in order to obtain the pure precursor spectrum and will also act as the primary proof-of-concept data. The initial flow rate of THF was fixed at 3 mL/min which was the nominal flow rate for an injector on the pilot MOCVD system. Nominal rates of argon gas flow were also used – 0.5 SLPM on the push and 2 SLPM on the shroud. The pressure saturated inside the gas cell at around 10 Torr. Gas cell window argon purge was maintained at around 0.5 SLPM for the entire duration of the experiment. Using higher values than this increased the absorbance of the IR beam inside the gas cell substantially and also created turbulence in the flow of gases inside the cell. Exposure time was kept at 10 seconds for all the spectra.

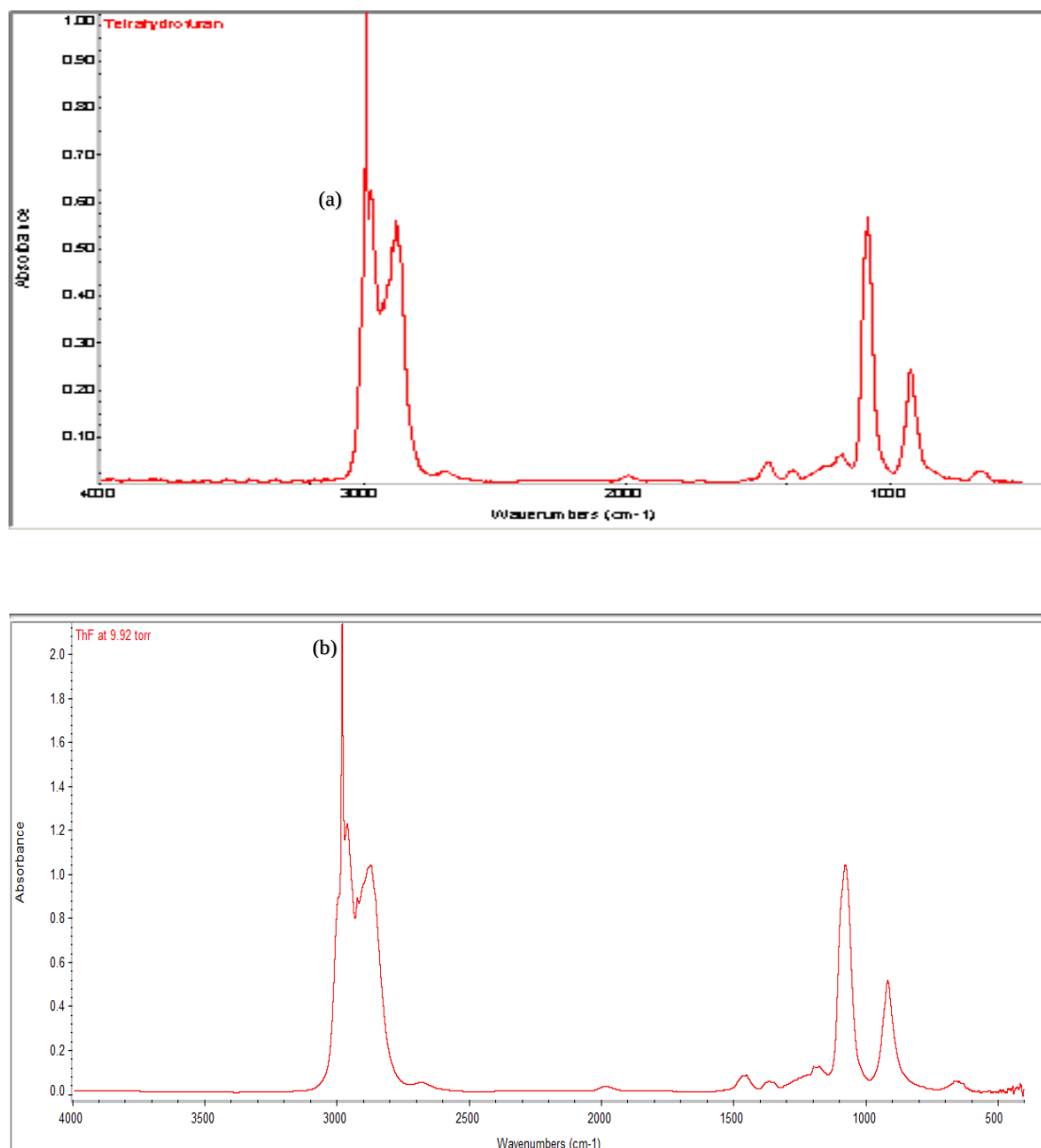


Figure 4.5 Spectrum of Tetrahydrofuran (a) Reference spectrum from Thermo-Scientific database (b) Obtained using inline gas cell at University of Houston.

It is clear from Figure 4.5 that the spectrum obtained for THF is identical to that published in the literature. The presence of Ar gas has an effect of IR beam absorbance as well. The spectrum in Figure 4.5 (a) is extracted from the Thermo Scientific database and its maximum peak intensity is normalized to 1.0 Absorbance Unit (A.U.). The data presented in Figure 4.5 (b) were obtained using the custom inline gas cell and are not normalized to the maximum but the features of the spectrum are remarkably the same. Peak indexing and

identification were not performed on this spectrum but will be presented for the precursor molecules.

Nominal quantities of precursor solutions were prepared by dissolving each of them in THF solvent. The molarity of the solution was kept at 0.2 Moles which was standard used in the pilot MOCVD system. But instead of preparing a cocktail solution, individual precursor solutions were prepared with nominal composition ratios of 0.6:0.6:2.0:2.3:0.15 (Gd:Y:Ba:Cu:Zr) to analyze the precursor molecules separately with the FTIR system. The first precursor molecule that was studied was Barium bis(2,2,6,6 - Tetramethyl - 3,5,heptanedionate) bis 1,10-phenanthroline ($\text{Ba}(\text{TMHD})_2\text{ph}_2$). For the initial experiment, the pressure inside the gas cell was varied systematically from 3 through 9 Torr to identify if the spectrum signal strength also showed a corresponding increase in its values.

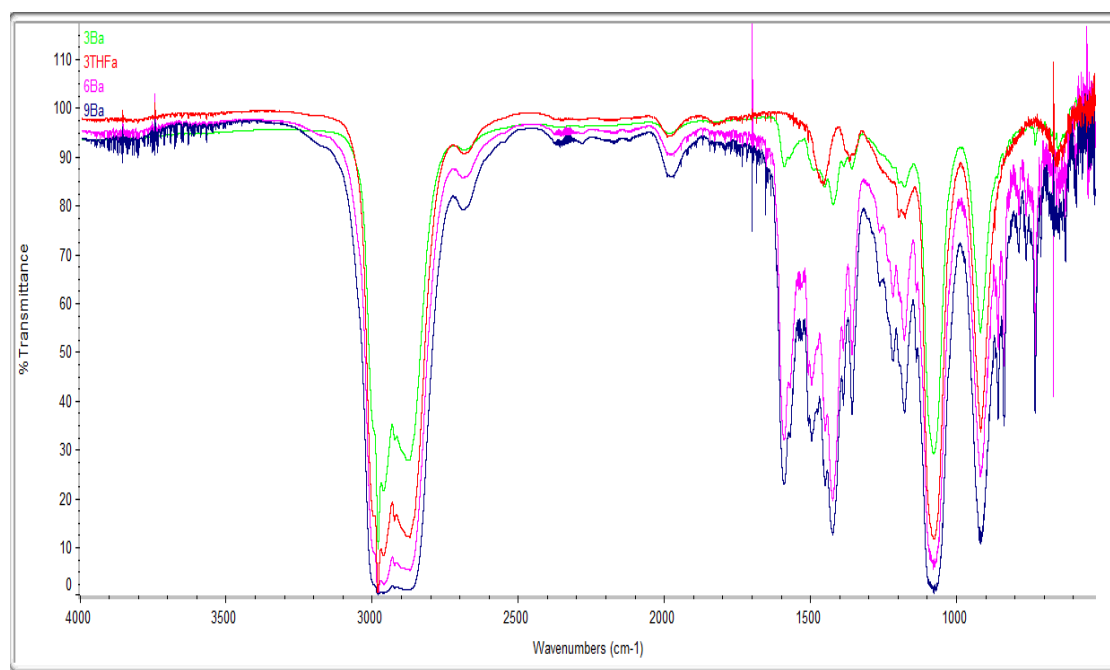


Figure 4.6 Transmission spectra of $\text{Ba}(\text{TMHD})_2\text{ph}_2$ obtained at 3, 6 and 9 Torr pressure maintained in the gas cell. The THF background spectrum obtained at 3 Torr is also shown.

The barium precursor spectra in Figure 4.6 were not background subtracted from the Tetrahydrofuran spectrum. It is clearly seen from Figure 4.6 that the peaks at 3000 cm^{-1} overlap with the THF peaks arising at around the same wavenumber. This is because the

barium precursor is being analyzed with the stream of Tetrahydrofuran solvent and argon carrier gas. But features of the barium spectrum unique to its molecular structure are evident around 1500 cm^{-1} where the THF peaks are almost absent. These are the peaks of interest in this study. Figure 4.7 is a close up of the same figure zoomed in the region of interest.

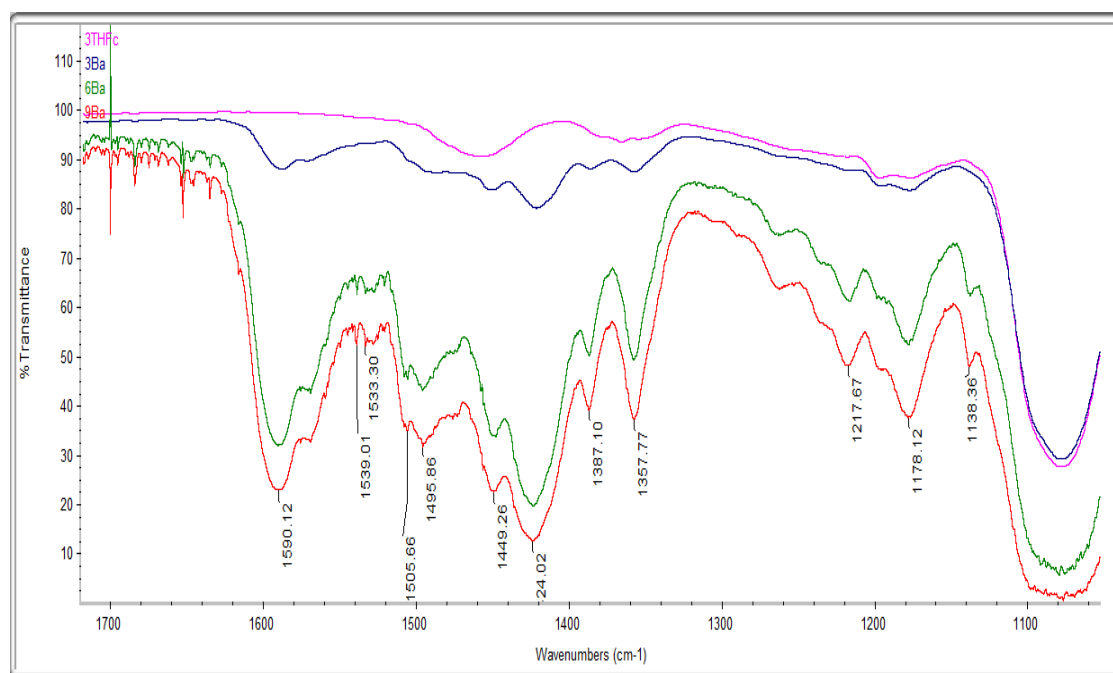


Figure 4.7 Zoomed-in region of $\text{Ba}(\text{TMHD})_2\text{ph}_2$ spectra between $1700 - 1000\text{ cm}^{-1}$ wavenumbers.

In Figure 4.7, it can be clearly seen from the highlighted region of interest (ROI) that there are a number of peaks of interest in the spectra of the barium precursor molecules that are absent from the THF spectrum even at 3 Torr of pressure. Ryu et al.[101] assign the peaks observed at 1590 cm^{-1} and 1533 cm^{-1} to a combination band frequency vibration arising from $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{O})$ stretching frequencies. The peak at 1389 cm^{-1} , slightly shifted to lower wavenumber of 1387.10 cm^{-1} in the present case, possibly due to the effect of argon carrier gas and THF as solvent[103,104], is assigned to $\nu(\text{C}-\text{CH}_3) + \text{ring deformation} + \nu(\text{MO})$ stretching frequencies. The preliminary peaks of interest for this study would be those involving $\nu(\text{MO})$ stretching frequencies since it is possible to track such peaks for cation concentration studies in the vapor stream. The stretching frequencies arising from the

metalorganic ligand might experience some overlap in the peak frequencies since tetramethyl heptanedionate(TMHD) is the primary ligand that is attached to all the cations. But by observing and tracking the $\nu(\text{MO})$ peaks that are unique to each cation, it is possible to quantitate fluctuations in cation concentration that might be observed in the vapor path due to inhomogeneous vaporization of the precursor molecules inside the evaporator.

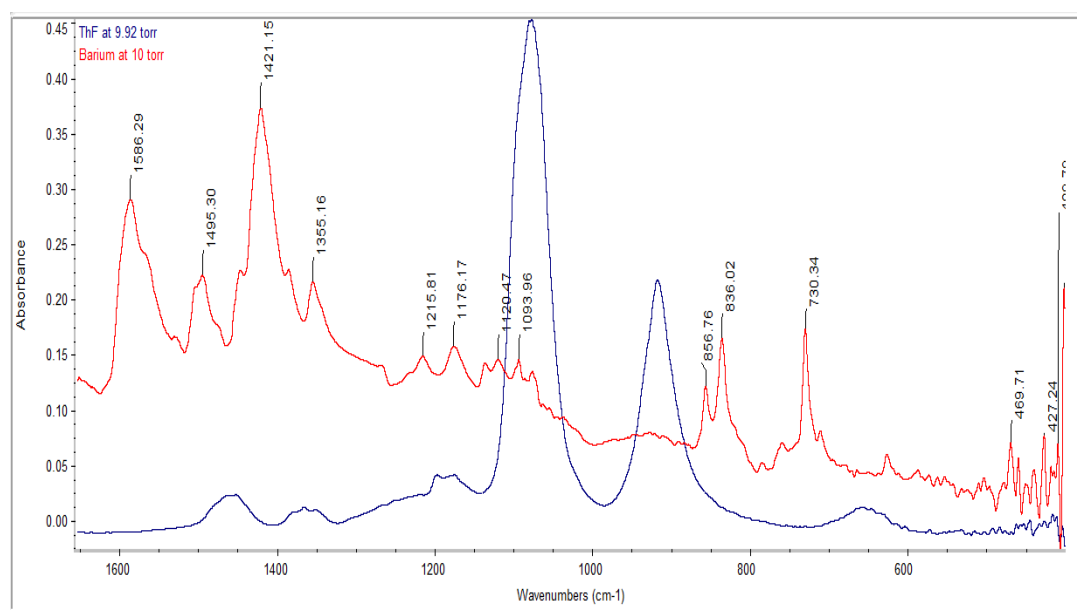


Figure 4.8 Absorption spectrum of $\text{Ba}(\text{TMHD})_2\text{ph}_2$ subtracted from THF as background.

Smaller peaks were also observed at 469 cm^{-1} and 427.24 cm^{-1} for the $\text{Ba}(\text{TMHD})_2\text{ph}_2$ absorption spectrum shown in Figure 4.8 which is background subtracted from the pure THF spectrum in Figure 4.8. The smaller peak at 469 cm^{-1} has been assigned to ring deformation + $\nu(\text{MO})$ [101]. Figure 4.8 displays this important low wavenumber peak that is attainable only with a special KBr window which is capable of transmitting down to 400 cm^{-1} (or $25\text{ }\mu\text{m}$ wavelength) with 100 % transmittance.

One of the main challenges of this study was finding sufficient background literature on this topic. The work of Ryu et al.[101] was conducted by analyzing the output from an inert TGA experimental setup without the phenanthroline group i.e., pure $\text{Ba}(\text{TMHD})_2$. This does not reflect the complex architecture of a real MOCVD system where the vaporization is

carried out in the presence of a solvent and a carrier gas which is known to affect the decomposition temperature of the precursor molecules. [103,104]. But, by systematically studying the individual precursor molecule and subtracting the spectrum from the corresponding parent ligand molecule, it is possible to infer the primary stretching frequency of each cation molecule which will be a unique signal that can be used for quantitative analysis.

Spectra of all the other precursor molecules were also successfully obtained except for copper since the windows fogged up by the time the copper molecules were flowing. Future studies need to be conducted to obtain more information on the primary parent ligand TMHD and subtract from each spectrum to obtain the unique fingerprint for each individual molecule.

Yttrium(III) tris(2,2,6,6,-tetra-methyl-3,5,-heptanedionate) ($\text{Y}(\text{TMHD})_3$) was the next molecule to be analyzed using the FTIR gas cell.

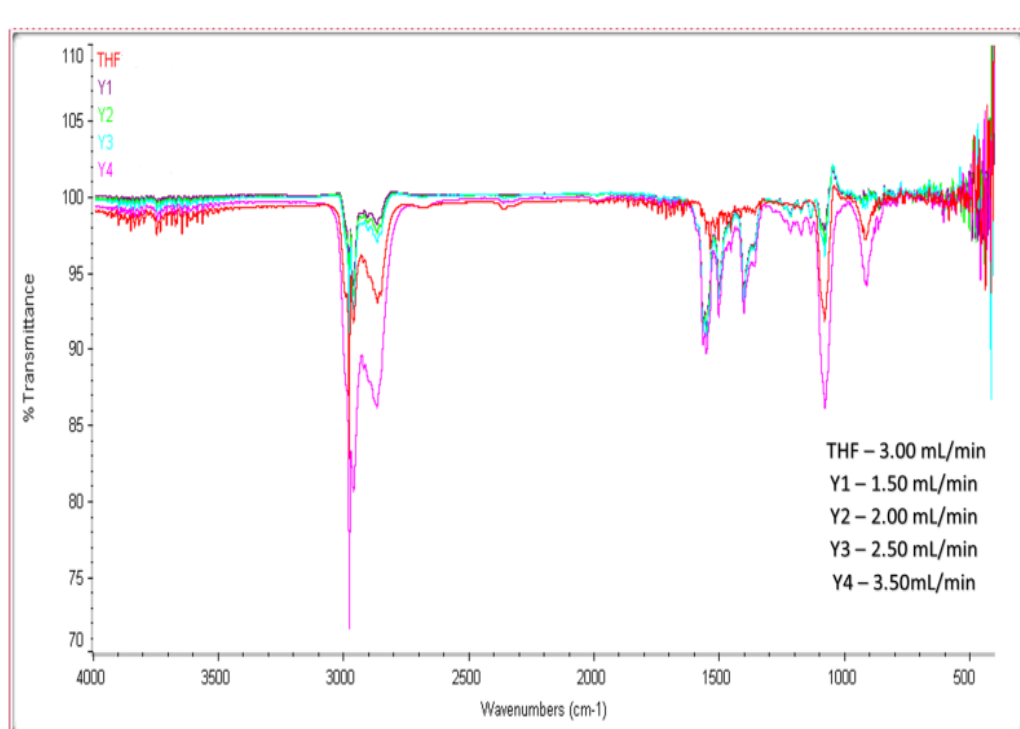


Figure 4.9 Full spectrum of $\text{Y}(\text{TMHD})_3$ precursor molecule with THF and Ar carrier gas.

The full spectrum of the $\text{Y}(\text{TMHD})_3$ precursor molecule was obtained with the THF solvent and Ar carrier gas with nominal flow rates for the shroud and the push shown in Figure 4.9. The rate of flow was increased in intervals of 0.50 mL/min to observe if the strength of the $\text{Y}(\text{TMHD})_3$ signal showed a corresponding decrease in the transmitted signal (due to increased absorbance of the incoming IR signal). The molecule behaves exactly like the barium molecule and Figure 4.9 establishes the fact that the flow rate of the yttrium precursor molecule can also be controlled in a fine manner by varying its input rate according to the IR signal strength that can be observed in the vapor stream in real time.

Figure 4.10 is a close up of the same spectrum in the 3150 cm^{-1} – 2300 cm^{-1} wavenumber range. In this range, it is clearly seen that the peaks overlap almost exactly with each other and all of these peaks can be attributed clearly to the vibrations of the THF molecule. Kovalgin et al.[92] attribute the peak at 2964 cm^{-1} to the C-H_x stretching of the tertiary butyl group, but since the $\text{Y}(\text{TMHD})_3$ spectra were not background subtracted from THF, there is significant overlap with the peaks arising from THF.

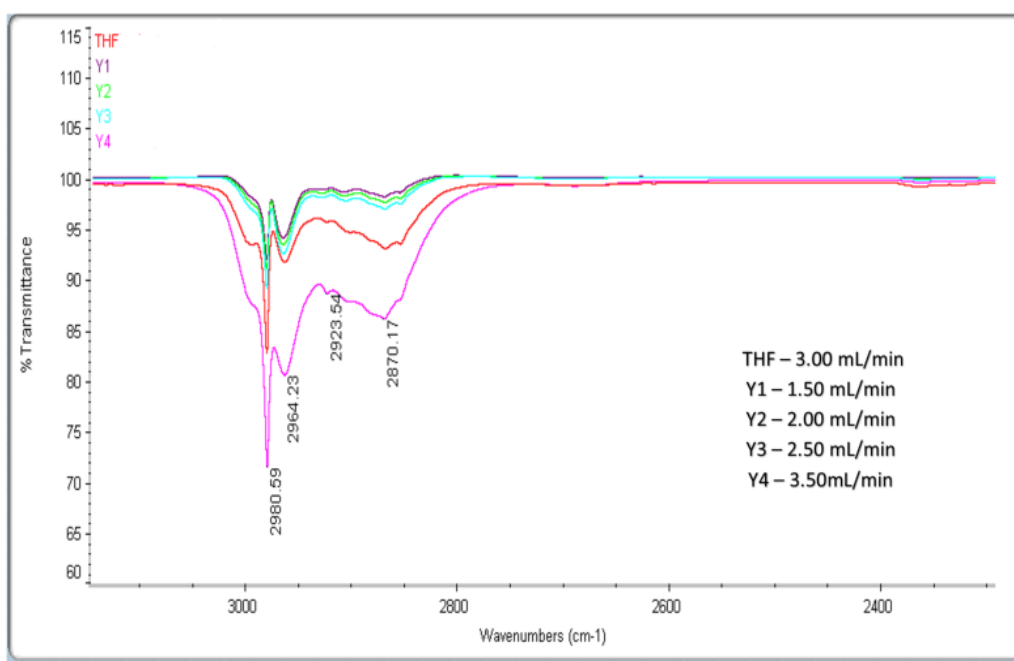


Figure 4.10 Zoomed-in snapshot of the $\text{Y}(\text{TMHD})_3$ spectrum in the $3150 - 2300\text{ cm}^{-1}$ range.

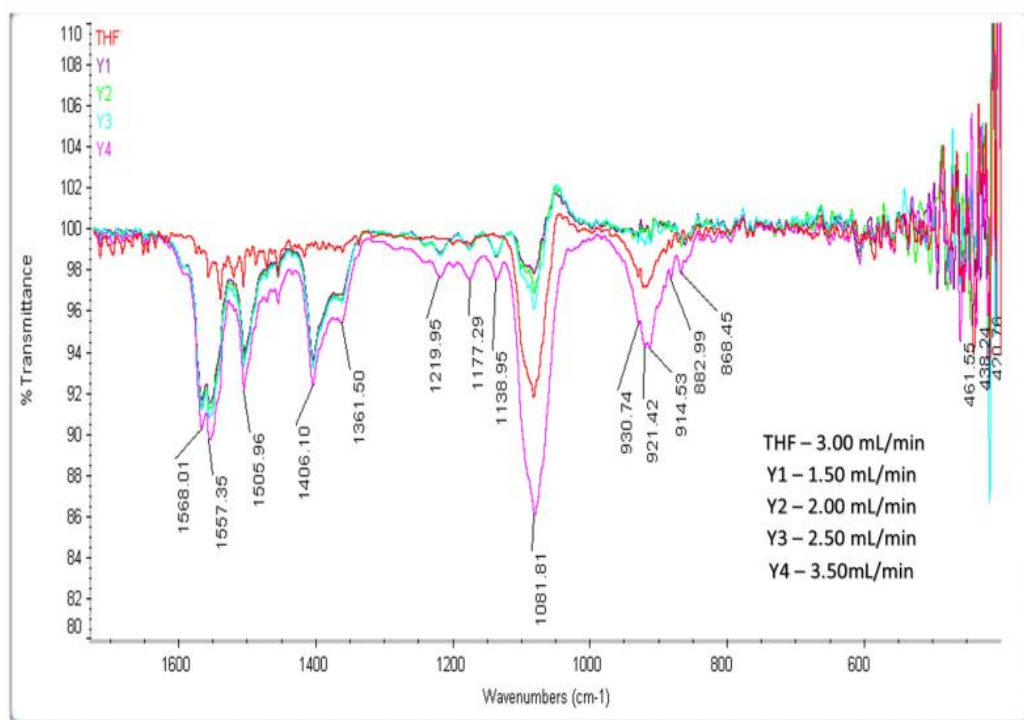


Figure 4.11 Zoomed-in snapshot of the $Y(TMHD)_3$ spectrum in the $1700 - 400\text{ cm}^{-1}$ range.

From Figure 4.11, it is clear that there are peaks in this ROI which are not contributed by the THF molecule but instead arise from the vibration of the $Y(TMHD)_3$ molecule. For example, the array of peaks from 1568 cm^{-1} through 1138 cm^{-1} are all seen in the $Y(TMHD)_3$ spectrum but not in the pure THF spectrum. Kovalgin et al. [92] attribute the peaks seen in the $1571 - 1556\text{ cm}^{-1}$ range to C=C or C=O stretching in the rings and the peaks at 1505 cm^{-1} and 1406 cm^{-1} to C = C ring stretching. No other peaks were identified due to lack of literature background, but further studies can be conducted to isolate the $\nu(MO)$ peaks which will be critical for real-time process control purposes. The peaks at the lower end of the wavenumbers below 500 cm^{-1} already show significant deterioration in signal-to-noise ratio due to precursor residual coating on the windows which severely affect the transmittance range of KBr windows.

Gadolinium tris (2,2,6,6, - tetramethyl - 3,5 - heptanedionate) ($Gd(TMHD)_3$) was the next molecule to be analyzed using the inline FTIR gas cell. No background literature exists on this molecule presently, although the stretching frequencies of the C-H bonds in the ring is

expected to be close to that seen for $\text{Y}(\text{TMHD})_3$. One of the major drawbacks in this setup that became apparent as time went on was the degradation of the signal quality below 500 cm^{-1} wavenumber. This will be addressed in the future version of the experiment with a well-engineered gas cell as explained later.

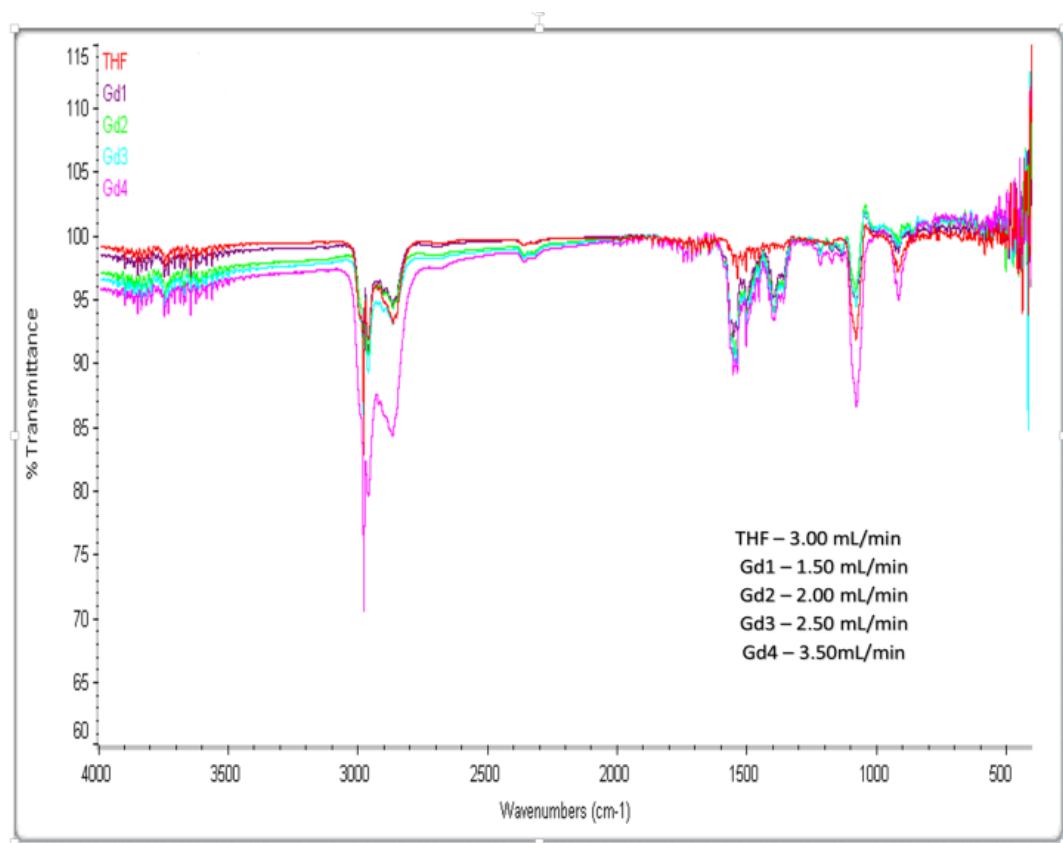


Figure 4.12 Full Spectrum of the $\text{Gd}(\text{TMHD})_3$ molecule obtained using inline FTIR gas cell.

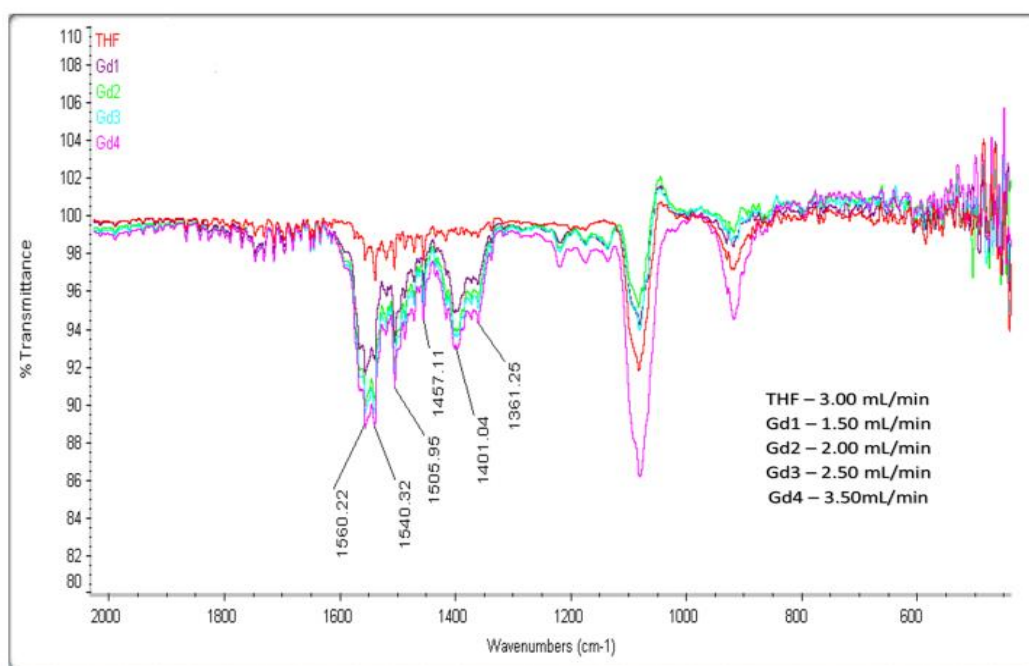


Figure 4.13 Zoomed-in snapshot of the Gd(TMHD)_3 molecule in the $2000 - 400 \text{ cm}^{-1}$ wavenumber range obtained using inline FTIR gas cell.

Zirconium tetrakis(2,2,6,6 - tetramethyl - 3,5 heptanedionate) (Zr(TMHD)_4) was the last compound to be analyzed using the inline FTIR gas cell. This precursor molecule usually has the lowest concentration in the vapor stream since it is added only as a dopant, usually between 5 – 15%. (0.15 in molar concentration ratio in this spectrum). Figure 4.14 is a snapshot of the entire spectrum of Zr(TMHD)_4 that was captured using the inline FTIR gas cell. Figure 4.15 highlights some of the peaks identified in the range of $2000 - 1600 \text{ cm}^{-1}$ wavenumber range that is unique to the Zr(TMHD)_4 molecule. The lower end of the spectrum is overrun with noise by this point due to substantial buildup of precursor residual coating. Figure 4.14 and Figure 4.15 show relatively lower transmission percentage when compared to other elements due to the lower concentration of Zr dopant in THF.

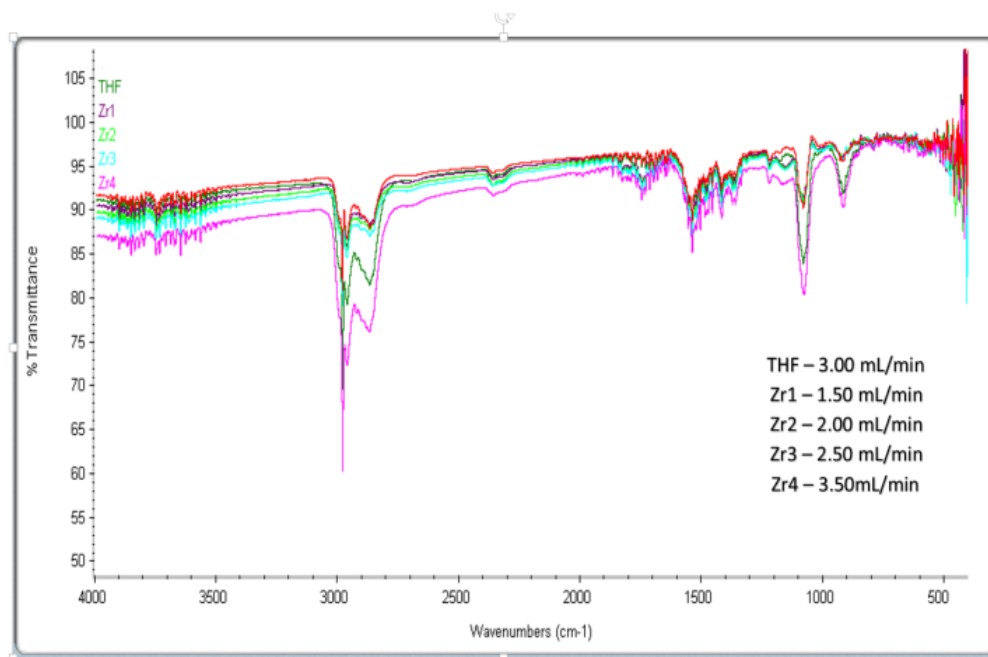


Figure 4.14 Full spectrum of the Zr(TMHD)_4 molecule with THD and Ar carrier gas.

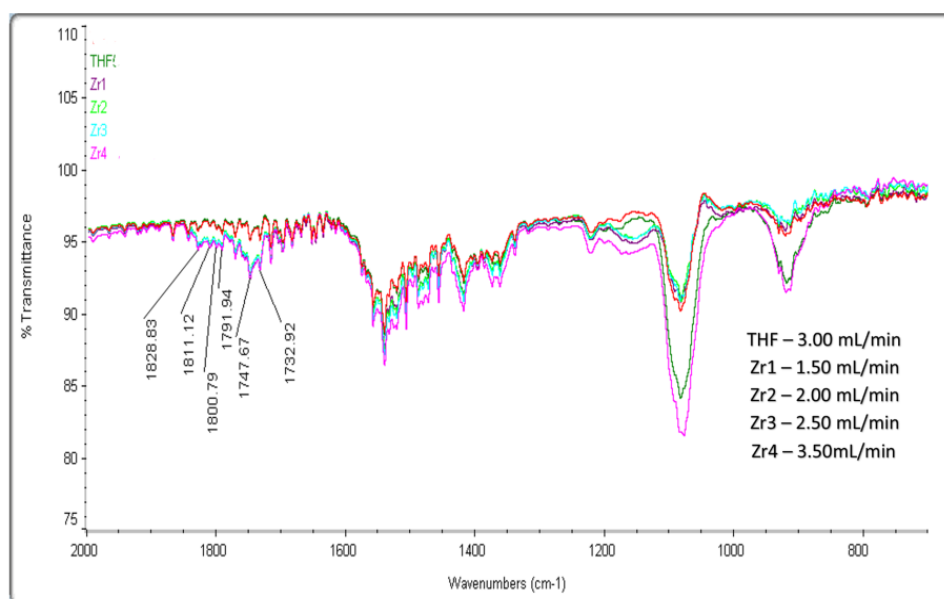


Figure 4.15 Zoomed-in snapshot of the Zr(TMHD)_4 spectrum in the range of $2000 - 750 \text{ cm}^{-1}$ wavenumber with peaks indexed in the 1850 cm^{-1} to 1700 cm^{-1} wavenumber range belonging Zr(TMHD)_4 molecule.

Cu(TMHD)_2 was the last precursor molecule that was supposed to be analyzed but by the time the precursor molecule started to flow through the gas cell, the entire window of the gas cell became coated with precursor residue as shown in Figure 4.16.



Figure 4.16 KBr window completely fogged up with precursor residual coating.

Analyzing the precursor coating on the window with no flow of gases shows it to be mostly composed of solid THF residue present due to the solvent and some barium residue presumably due to the higher decomposition temperature of the barium precursor molecule which renders it stable despite repeated washouts with THF.

A more robust, well-engineered commercial sampling cell with window purging technology can be purchased and installed inline for real-time FTIR analysis which would solve most of the issues that were experienced with the custom setup. Figure 4.17 is one such setup that is available in the market for gas analysis.

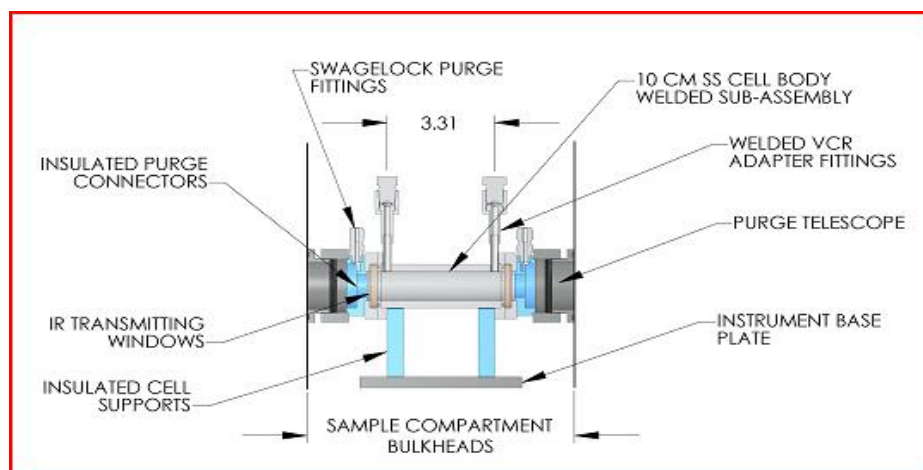


Figure 4.17 Commercial gas analysis cell.

The Thermo-Scientific IG 50 would be an excellent candidate as a FTIR instrument since it has an optional external detector that can be detached from the instrument and kept at a safe distance away from the heated lines to track the vapor stream composition remotely. All the scans presented in this thesis were performed with a Thermo-Scientific IG 50 base demo model.



Figure 4.18 Thermo-Scientific IG 50 with external detector module.

A simple feedback loop control circuit has also been proposed with individual injectors controlling the flow of precursor to the vaporizer unit depending upon the strength

of the IR signal observed with an inline gas cell. Figure 4.19 shows a schematic of this feedback control loop.

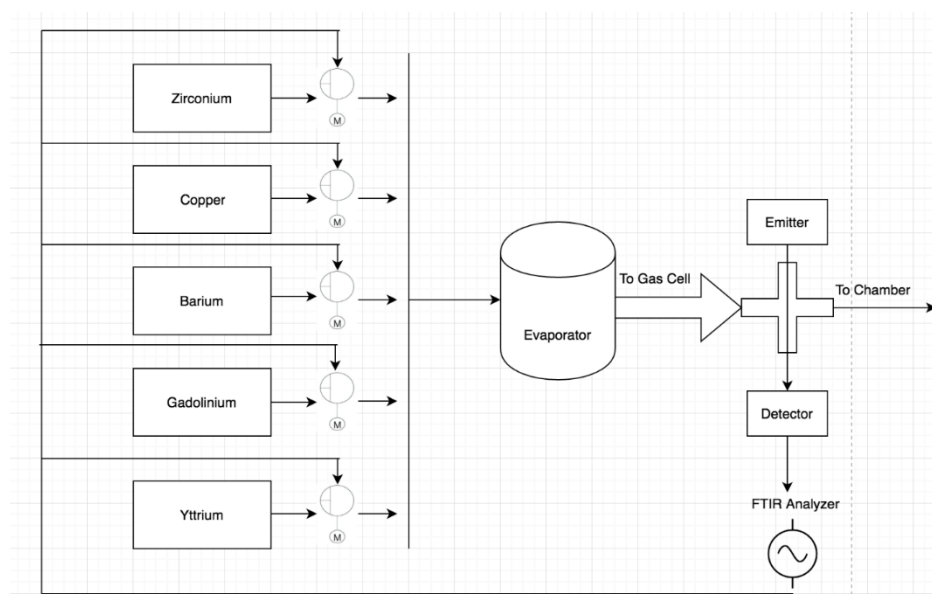


Figure 4.19 Schematic for MOCVD process control via Feedback loop mechanism.

A simple feedback loop mechanism for precursor concentration control in the vapors is suggested in Figure 4.19. Separate injector and liquid mass flow controller (which is already available in the Advanced Pilot MOCVD setup) for individual precursor components suspended in THF solvent is a prerequisite.

Stoichiometric ratios of the various precursor molecules are injected into the evaporator using the metering pumps. The gas stream is then analyzed using the gas cell located downstream before the chamber. Real-time analysis of the data is carried out using the FTIR instrument, which continuously monitors the vapors.

Any sudden changes in composition of the vapors (either due to inhomogeneous vaporization of precursor molecules or changing reactor parameters over time) can be readily

detected and the FTIR can send out a signal requesting either increase or decrease of the flow of individual precursor molecules to maintain the vapors at the optimized concentration levels.

Chapter 5

Inductively Coupled Plasma – Mass Spectroscopy (ICP – MS)

The Inductively Coupled Plasma – Mass spectrometer (ICP – MS) is routinely being used by the superconductor manufacturing group at the University of Houston to determine thin film composition and for elemental analysis. Substantial improvements in measurement quality, reproducibility and quality control were undertaken as a part of this thesis work.

5.1.1. Instrumentation and Measurement methods:

The ICP – MS instrument used throughout the entirety of this thesis was the Agilent 7700 ICP – MS. The details of the instrument have already been provided in Chapter 2. Hardware details pertaining to the measurement procedure will be elucidated in this section.

The primary mode of measurement used in this ICP was internal standardization. It is a classic procedure to eliminate physical interferences that might arise from high matrix concentration. With this method of correction, a small group of elements (usually at ppb levels) are spiked into the sample, calibration standards and blanks to correct for variations in the response of the elements caused by the matrix. As the intensity of the internal standards change, the element responses are updated every time a sample is analyzed. It is important to consider the following points while choosing an appropriate standard for the measurements:

- 1) They are not present in the sample.
- 2) The sample matrix or analyte elements do not spectrally interfere with them.
- 3) They are usually grouped with analyte elements of a similar mass range. For example, a low mass internal standard is grouped with the low mass analyte elements.
- 4) Their ionization potential should be similar to that of the groups of analyte elements so they behave in a similar manner in the plasma.

The internal standard solution used in the present case was ^{115}In (Indium 115 a.m.u). This was chosen since its mass is within the range of those of the given elements of interest

(Cu,Y,Zr,Ba,Y)). Figure 5.1 is a photo showing the sample line, ISTD line and drainage line on the peristaltic pump setup.

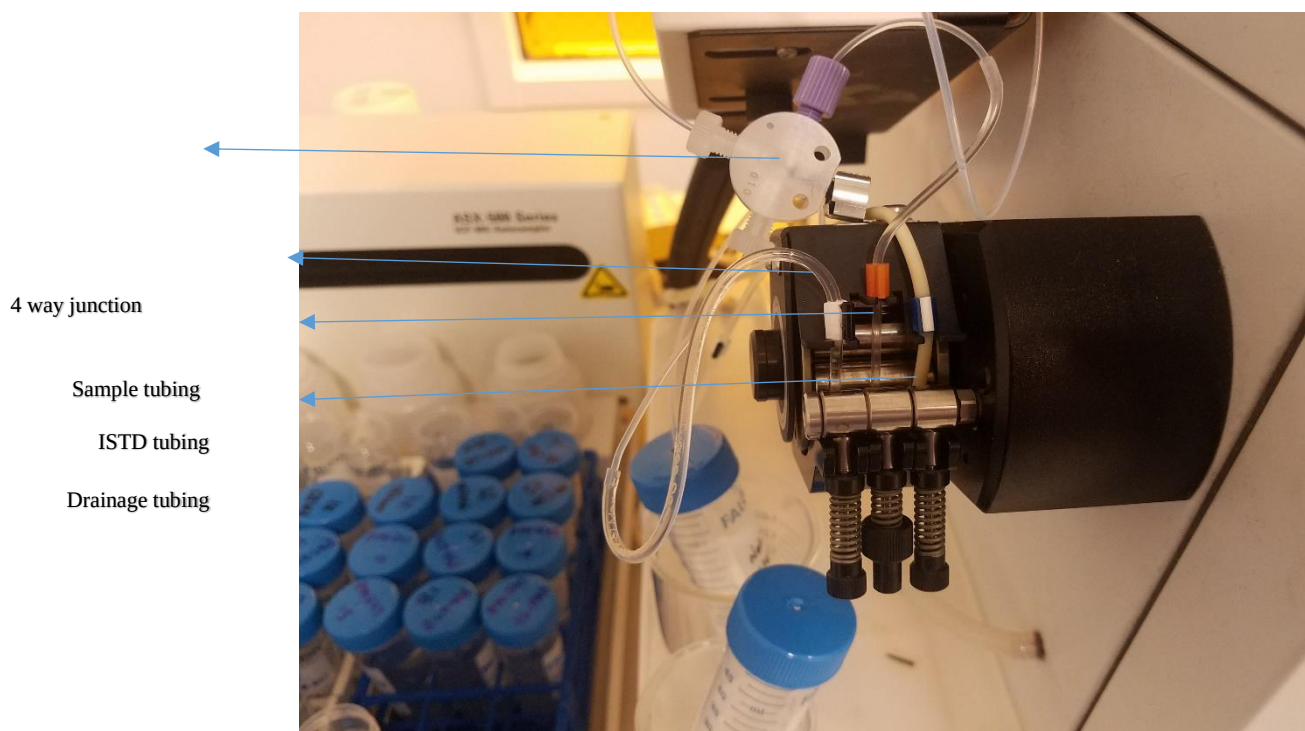


Figure 5.1 Photograph of the peristaltic pump setup with sample tubing, ISTD and draining tubing marked.

When a large number of samples are being measured in a batch for long durations of time, internal standardization compensates for sensitivity drift due to matrix components slowly blocking the sampler and skimmer cone orifices. In this method, the analyte signal drift is corrected by the signal of another element (the internal standard element) added to both the standard solution and the sample. If the signal of the analyte is affected for any of the above reasons, the internal standard element should also be affected in the same way, therefore the ratio of analyte to internal standard element is not affected. When the signals of the blank, standard solution, and the sample are **a0**, **a1**, **a2**, **a3** and **as**, and the signals of internal standard in each solution are **b0**, **b1**, **b2**, **b3** and **bs**, then the vertical and horizontal axes of the calibration curve are the a to b ratio and the concentration as shown below in Figure 5.2. When the ratio of the sample is **as/bs**, the concentration of sample **cs** can be calculated according to the calibration curve.

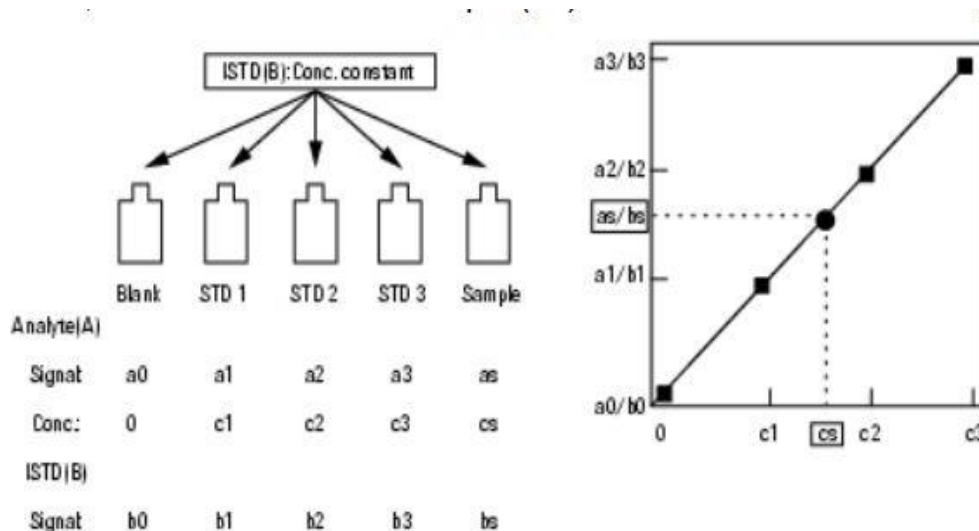


Figure 5.2 Method of internal standardization measurement. [105]

So in order to carry out measurements over a wide range of concentrations, standard solutions of all the elements of interest have to be prepared from 1 PPB to 25 PPM. 1000 $\mu\text{gm/ml}$ standard solutions are purchased from a commercial supplier and a cocktail solution is then prepared in a single vial from which all the solutions are prepared by means of serial dilution.

5.1.2. Octopole Reaction System (ORS) cell

The detection capability of traditional quadrupole mass analyzers for some critical elements is severely compromised by the formation of polyatomic spectral interferences generated by either argon, solvent, or sample-based ionic species. Although there are ways to minimize these interferences — including correction equations, cool plasma technology, and matrix separation — they cannot be completely eliminated. However, a new approach called collision/reaction cell technology has recently been developed that virtually stops the formation of many of these harmful species before they enter the mass analyzer.

The ORS system that was installed in the Agilent 7700 ICP MS was run in collision mode. Collision mode uses a non-reactive gas (He in this case) and a process called kinetic energy discrimination (KED) to selectively attenuate all polyatomic interferences based on their size. KED exploits the fact that all polyatomic ions are larger than analyte ions of the

same mass, so they collide with the cell gas more often as they pass through the cell, emerging with lower residual energy. These low energy ions are excluded from the ion beam by a bias voltage at the cell exit. Figure 5.3 is a schematic explaining this process.

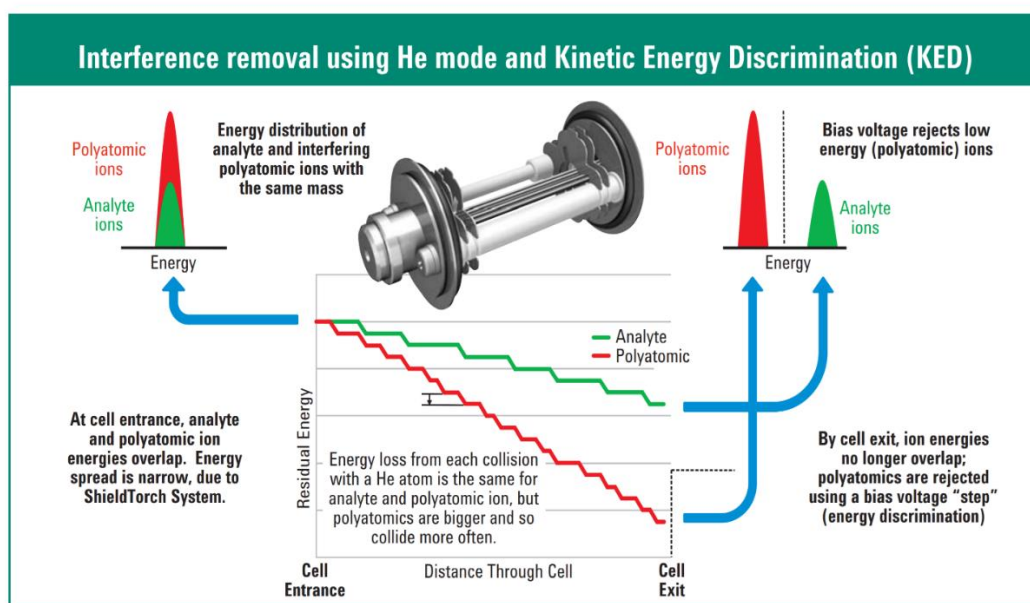


Figure 5.3 Schematic of Kinetic Energy Discrimination mode (KED) mechanism using He gas in the Octopole Reaction System (ORS) cell. [106]

Table 5.1 lists some of the potential polyatomic interferences that could interfere with accurate analysis of cations found in REBCO thin film.

Table 5.1 List of cations of interest in REBCO thin film analysis with potential interfering polyatomic species with same mass to charge ratios. [107]

Isotope	Abundance	Interference
^{130}Ba	0.106	$^{98}\text{Ru}^{16}\text{O}_2^+$
^{132}Ba	0.101	$^{100}\text{Ru}^{16}\text{O}_2^+$
^{134}Ba	2.417	$^{102}\text{Ru}^{16}\text{O}_2^+$
^{136}Ba	7.854	$^{104}\text{Ru}^{16}\text{O}_2^+$
^{209}Bi	100.	$^{193}\text{Ir}^{16}\text{O}^+$
^{63}Cu	69.1	$^{31}\text{P}^{16}\text{O}_2^+$, $^{40}\text{Ar}^{23}\text{Na}^+$, $^{47}\text{Ti}^{16}\text{O}^+$, $^{23}\text{Na}^{40}\text{Ca}^+$, $^{46}\text{Ca}^{16}\text{O}^1\text{H}^+$, $^{36}\text{Ar}^{12}\text{C}^{14}\text{N}^1\text{H}^+$, $^{14}\text{N}^{12}\text{C}^{37}\text{Cl}^+$, $^{16}\text{O}^{12}\text{C}^{35}\text{Cl}^+$
^{65}Cu	30.9	$^{49}\text{Ti}^{16}\text{O}^+$, $^{32}\text{S}^{16}\text{O}_2^1\text{H}^+$, $^{40}\text{Ar}^{25}\text{Mg}^+$, $^{40}\text{Ca}^{16}\text{O}^1\text{H}^+$, $^{36}\text{Ar}^{14}\text{N}_2^1\text{H}^+$, $^{32}\text{S}^{33}\text{S}^+$, $^{32}\text{S}^{16}\text{O}^{17}\text{O}^+$, $^{33}\text{S}^{16}\text{O}_2^+$, $^{12}\text{C}^{16}\text{O}^{37}\text{Cl}^+$, $^{12}\text{C}^{18}\text{O}^{35}\text{Cl}^+$, $^{31}\text{P}^{16}\text{O}^{18}\text{O}^+$
^{155}Gd	14.8	$^{139}\text{La}^{16}\text{O}^+$
^{157}Gd	15.68	$^{138}\text{B}^{19}\text{F}^+$, $^{141}\text{Pr}^{16}\text{O}^+$
^{177}Hf	18.5	$^{161}\text{Dy}^{16}\text{O}^+$

It can be seen from Table 5.1 that a significant number of polyatomic species exists that can interfere with the barium, gadolinium and copper cations. A number of solutions containing a wide range of cations is used for tuning the Agilent 7700 ICP MS: Pulse/Analog(P/A) tuning solution for tuning the detector, ICP MS stock tuning solution for tuning the quadrupole mass analyzer, Internal standard solution for ISTD reference signal. No Ruthenium is fortunately present in any of the solutions. However, a 1 percent HNO_3/HCl solution is used as stand-by cleaning solution for the system and the skimmer cone has a fine coating of calcium deposited on it for longevity, so $^{46}\text{Ca}^{16}\text{O}^1\text{H}^+$ is potentially an ionic species that might be formed during plasma activity. Moreover, intermittent ionic species like $^{36}\text{Ar}^{12}\text{C}^{14}\text{N}^1\text{H}^+$ and $^{14}\text{N}^{12}\text{C}^{37}\text{Cl}^+$ are capable of forming just by virtue of running the plasma with an argon carrier gas in atmosphere. So there is substantial potential for the $^{63}\text{Cu}^+$ ion to suffer polyatomic interferences with the aforementioned species mentioned in the literature. It should also be mentioned that the final useful metric from the ICP MS data is relative concentration of all the cations normalized to 100 percent, in which case, substantial noise in

one of the cation concentration measurements will cause the other cation percentages to vary as well (though the total error should remain the same). Table 5.1 is also not a comprehensive list so there could potentially be other species not mentioned in this reference. [107]

The ORS system was installed and Octopole RF voltage, KED bias voltage and Helium gas flow rate were setup with assistance from Agilent. Since the aforementioned advantages clearly outweighed any potential disadvantages and the signal-to-noise ratio of the system was not affected negatively, no systematic experiments were conducted in a sequential fashion to study the influence of this setup. However, reference data are available for four runs of the reference samples before installation of ORS and can be compared with four runs after the ORS system was installed. The same standard solutions were used with no major intervening maintenance protocols performed on the machine. It should be pointed out that the ICP MS is a very complicated instrument and its performance does degrade with time due to the destructive nature of the sample evaluation and acidic solutions used in the setup.

Nevertheless, the improvements in the standard deviations of the composition of the same samples measured during different experiments before and after the setup clearly point to an improvement in the measurement accuracy and reproducibility. An argument could also be made in favor of such data that, despite day-to-day variations in instrumental condition over time, reduction in standard deviation of measurements of the same samples points to a more practical performance metric of instrumental error reduction as opposed to a single set of experiments comparing the two modes sequentially.

Table 5.2 lists the average values obtained after four measurements of three references in both the modes.

Table 5.2 Average values of reference sample concentration in atomic percentage (at. %) measured over four runs. Standard deviation data is published in Figures 5.4 – 5.6 in lieu of error percentages.

Sample name	Cu	Y	Zr	Ba	Gd
Commercial tape (M4) Reference - Before ORS	51.4	8.9	0.9	30.2	8.5
PM 206 2 - Before ORS	46.5	9.6	1.6	32.2	10.0
PM 206 3 - Before ORS	46.5	9.8	1.7	31.7	10.3
Commercial tape (M4) Reference - After ORS	51.6	8.6	0.9	30.5	8.4
PM 206 2 - After ORS	46.4	9.5	1.5	32.3	10.3
PM 206 3 - After ORS	46.7	9.5	1.5	32.2	10.2

While the data in Table 5.2 look approximately close to each other at first glance and some of the variations seem quite nominal, Figures 5.4 – 5.6 present the standard deviations in every elemental composition of the three reference samples over four runs.

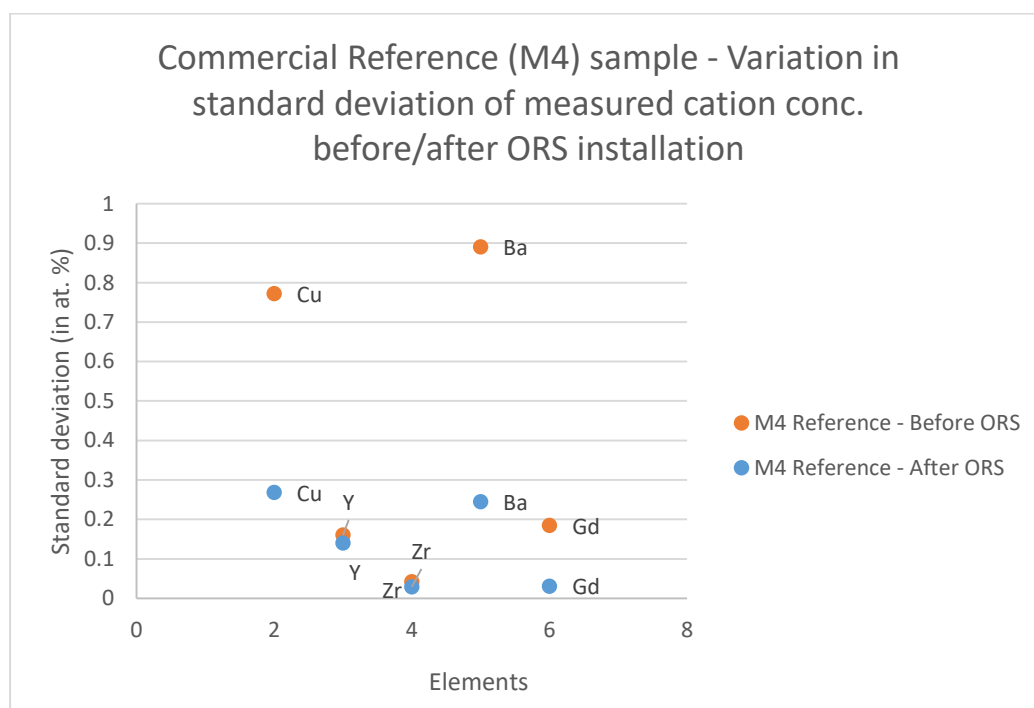


Figure 5.4 M4 Reference sample - Variation in standard deviation of measured cation concentration of samples from four runs before/after ORS installation.

Figure 5.4 shows the variation in the standard deviation of the measured individual cation atomic percentages before/after ORS cell installation over eight runs for the M4 sample. It can be clearly seen that standard deviation in barium concentration for the M4 sample drops from 0.9 % to 0.25 %. This is a substantial reduction in the dispersion of measured data. With the advent of machine learning techniques being utilized at the University of Houston to correlate thousands of samples across metrics like (Ba+Zr)/Cu ratios (which are being used up to three decimal places of accuracy) with nanorod dimension and lift factors, the ability to discern fine differences and measure samples with minimal drift is of paramount importance. Cu also shows substantial reduction from 0.78% to 0.26%. Gd shows a marginal improvement from 0.18 % to 0.03% while Zr and Y remain the same.

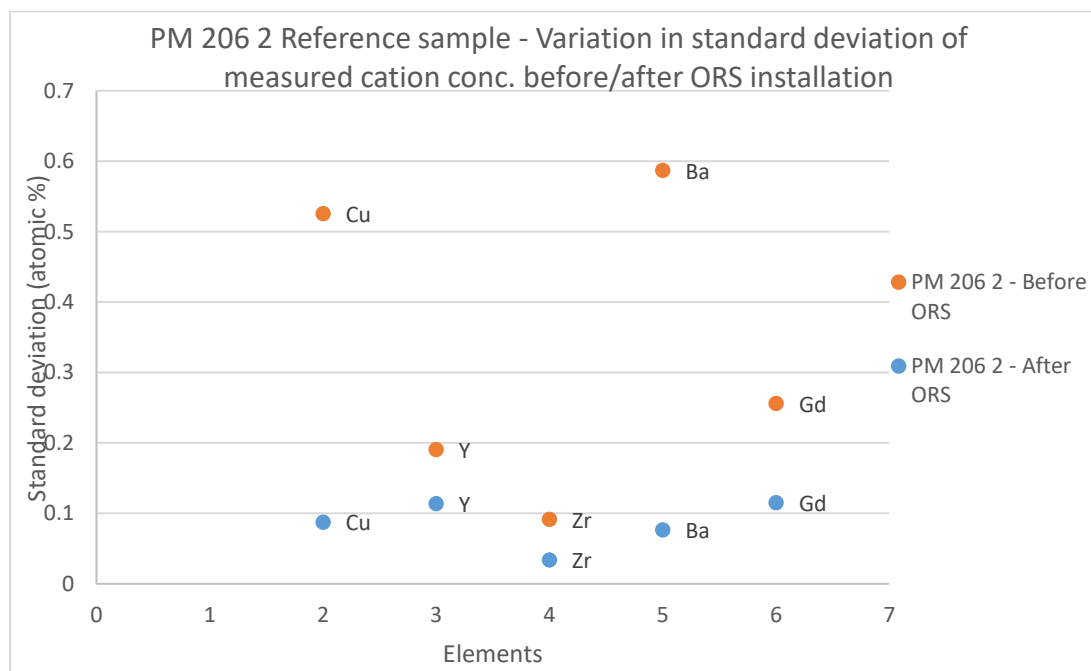


Figure 5.5 PM 206 2 reference sample - Variation in standard deviation of measured cation concentration of samples from four runs before/after ORS installation.

PM 206 2 shows similar substantial reduction in the standard deviation of measured concentration atomic percentages of copper, barium and gadolinium but in this case, yttrium and zirconium also show smaller reduction of nearly 0.05 atomic percent. The measured values with the ORS cell installed match more accurately with the expected film

concentration and stoichiometry of the precursors than that seen earlier for the Advanced MOCVD samples.

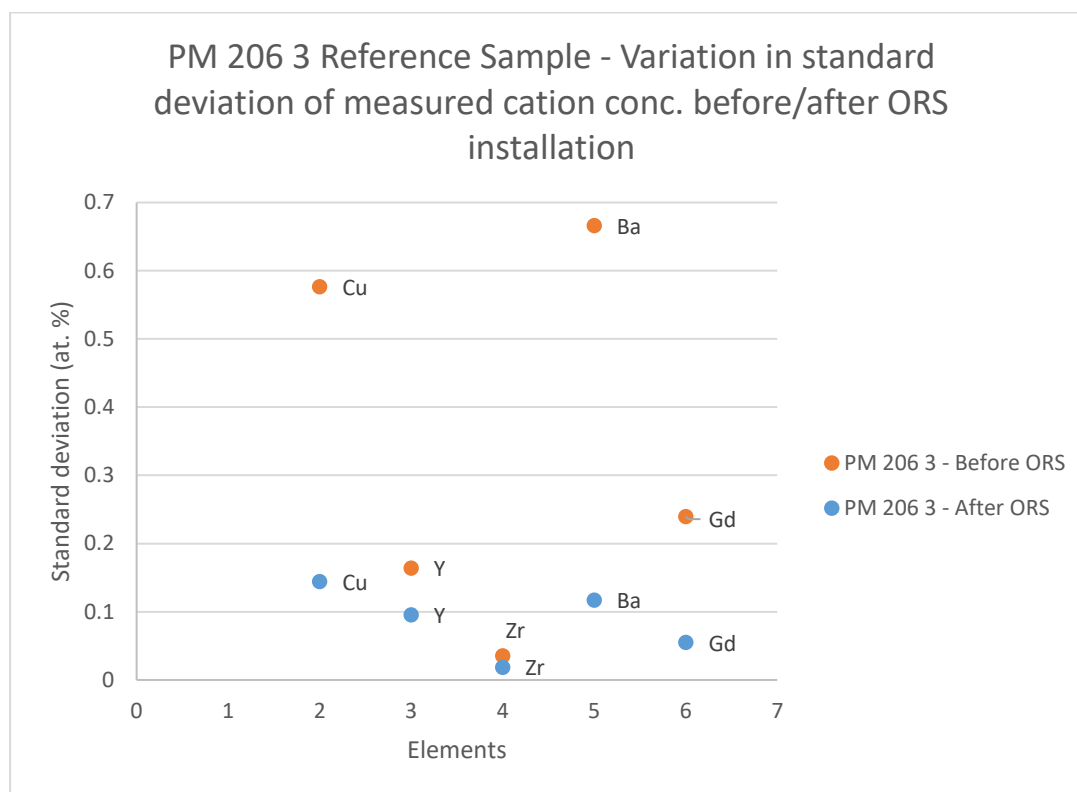


Figure 5.6 PM 206 3 reference sample - Variation in standard deviation of measured cation concentration of samples from four runs before/after ORS installation.

Similar results have been observed for copper, barium and gadolinium, with smaller reductions for yttrium and zirconium in PM 206 3 which is similar to that observed for the earlier samples. The ICP MS is now run in He gas mode with KED turned on by default due to the proven performance improvement it brings to reproducibility and repeatability of measurements.

5.1.3. Calibration and Curve fitting

The method of internal standardization (which was explained earlier) is the primary mode of concentration measurement in the ICP MS. In order to execute this mode of measurement, a set of standards from 1 PPB to 25 PPM were prepared. Individual cation standards are purchased from SpexCertiPrep with concentrations of 1000 $\mu\text{g/mL}$ in 2 percent

HNO₃ and a cocktail solution of 50 PPM dilution is prepared from which all the other standards are obtained by means of serial dilution. Figure 5.7 – 5.12 shows the conventional linear fitting that was applied to all the standards. A linear regression fit with a blank offset was conventionally applied to all the cations under consideration. Two modes were used in this method - blank offset where the blank solution is a 2 percent nitric acid solution and the curve is forced to pass through that point as the origin or (as Figure 5.7 shows for the copper cation) force through origin where the linear curve is forced to pass through the origin. This was left to the discretion of the operator and was to be decided depending upon which method produced the least errors that was seen in the fit for the individual cations.

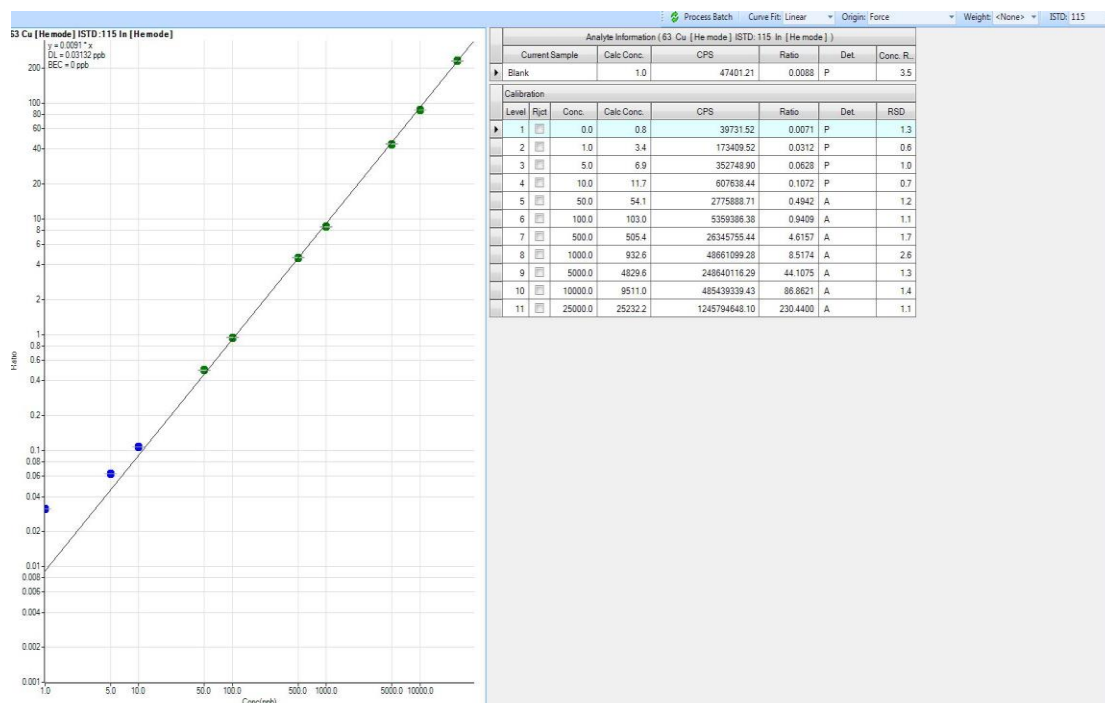


Figure 5.7 Linear fitting for copper cation concentration in the standard solutions from 0 PPB to 25 PPM.

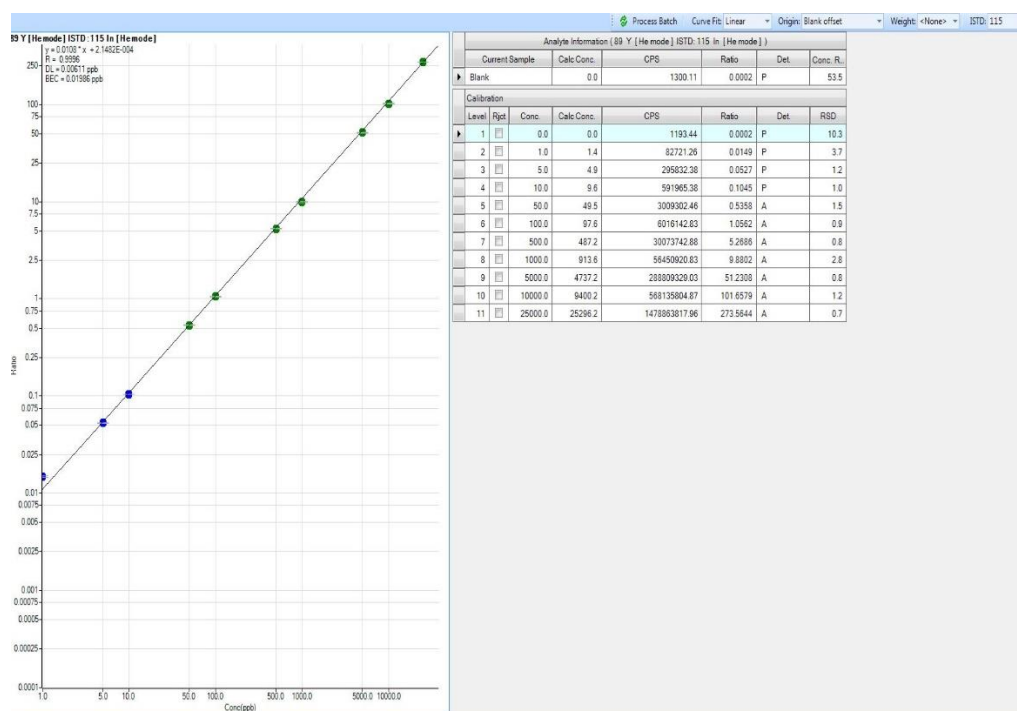


Figure 5.8 Linear fitting for yttrium cation concentration in the standard solutions from 0 PPB to 25 PPM.

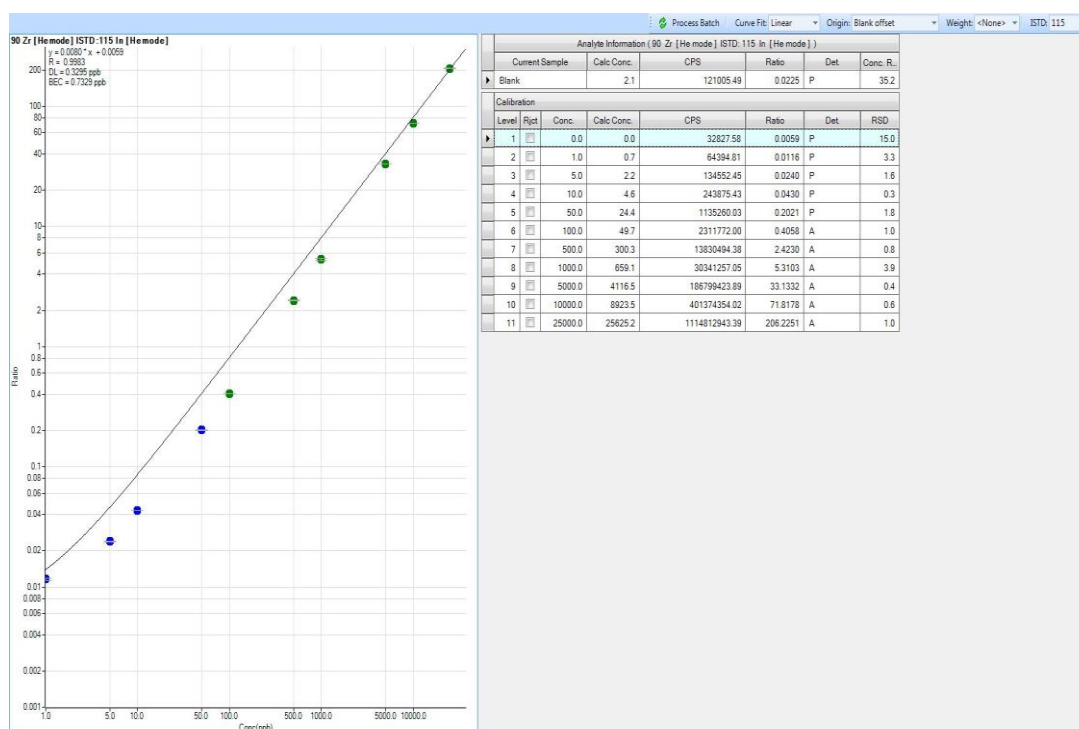


Figure 5.9 Linear fitting for zirconium cation concentration in the standard solutions from 0 PPB to 25 PPM.

Figure 5.9 was a special case observed in the zirconium cation concentration behavior where a linear trend was not predictable at all despite multiple attempts with different batches

of zirconium standards as starting material for the precursor standard solutions. The standards were also prepared and tested by chemists at the Earth and Geosciences analytical chemistry labs at University of Houston in a triple quadrupole Agilent 8800 ICP MS and exhibited the same kind of behavior. The vendor was contacted and assurance was given that no changes had been made to the procedures involving the fabrication of the zirconium standards which used to produce relatively decent linear fits equivalent to the other standards. The reason behind this kind of behavior remains unknown. It should be noted that 1 ml of each standard is initially extracted from every individual standard bottle of 1000 $\mu\text{g/mL}$ concentration and mixed into a vial which is made up to 20 mL with 2 percent nitric acid to generate a cocktail with 50 PPM concentration. All the other solutions are then generated from this master cocktail solution. So the number of pipetting steps where each standard bottle is actually involved is only one. So poor pipetting techniques during serial dilution cannot be the reason attributed to the behavior of the zirconium cation concentration since that would entail that the other cations also exhibit such nonlinear behavior which they do not.

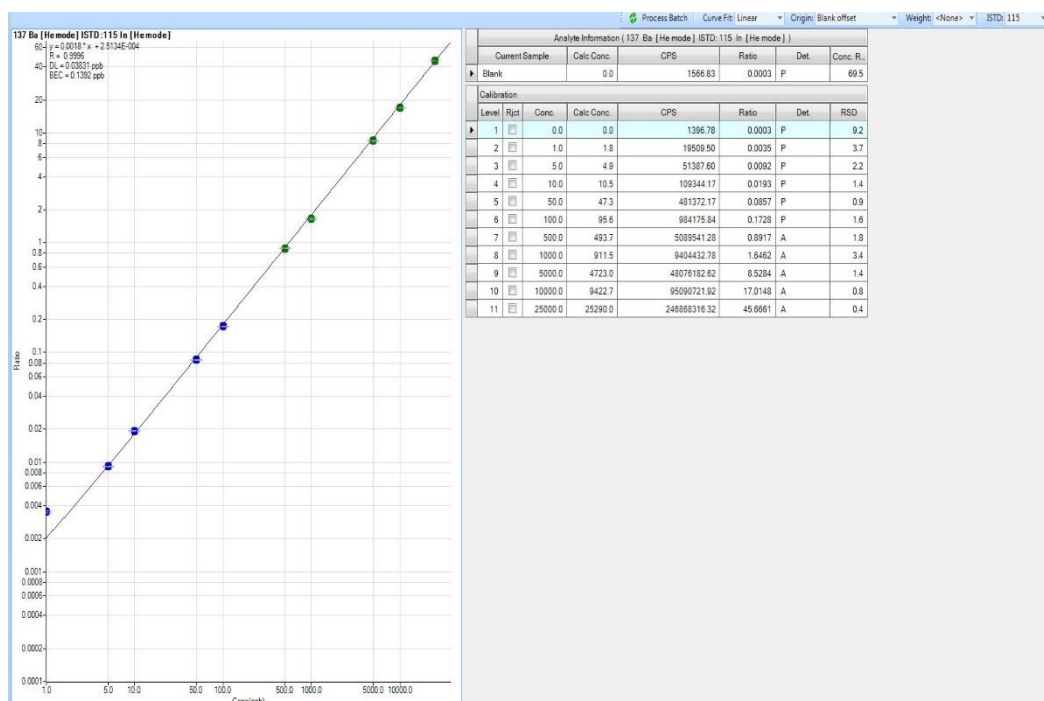


Figure 5.10 Linear fitting for barium cation concentration in the standard solutions from 0 PPB to 25 PPM.

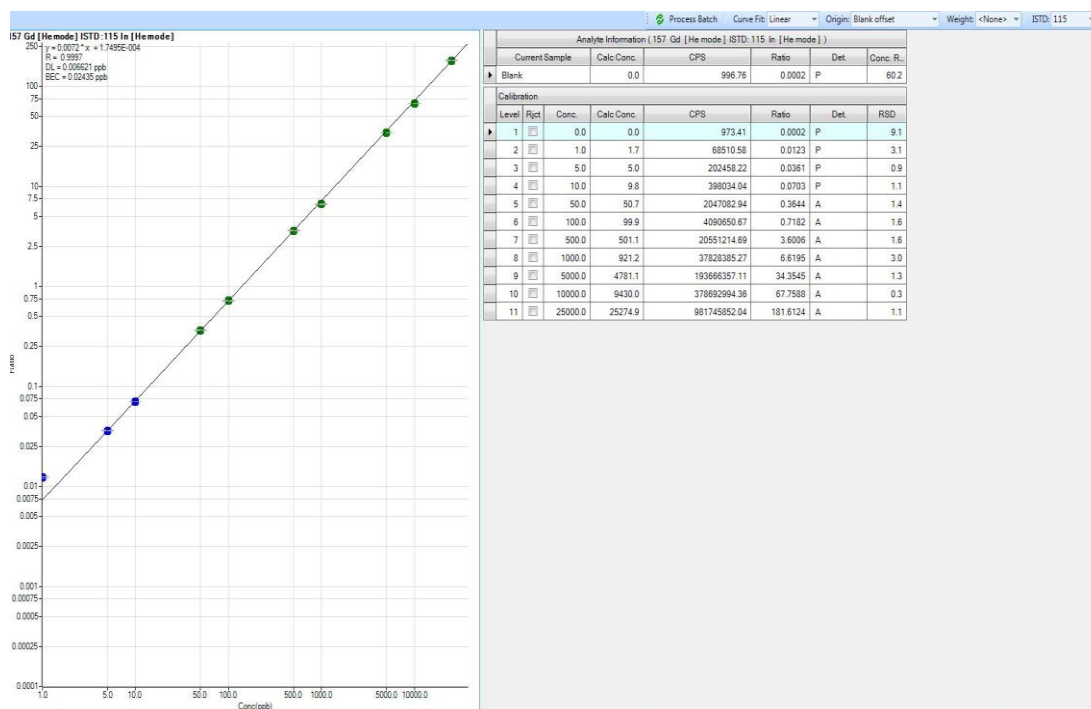


Figure 5.11 Linear fitting for gadolinium cation concentration in the standard solutions from 0 PPB to 25 PPM.

Table 5.3 displays the error percentages obtained from the linear fitting curves for all the cations except zirconium which has such a high percentage of error that it cannot be used for any practical measurement purposes and is not included here.

Table 5.3 Table of error percentages in measured cation concentration of standard solutions using linear fitting parameters.

Cation	1	5	10	50	100	500	1	5	10	25 ppm
	ppb	ppb	ppb	ppb	ppb	ppb	ppm	ppm	ppm	
Cu	240	38	17	8.2	3	1.08	6.74	3.408	4.89	0.9288
Y	40	4	4	1	2.4	2.56	8.78	5.256	6	1.1848
Ba	80	2	5	5.4	4.4	1.26	8.85	5.54	5.773	1.16
Gd	70	0	2	1.4	1	0.22	7.88	4.378	5.7	1.0996

Figures 5.12 – 5.16 display the plotted values of error percentages of the measured cation concentration in the standard solutions using linear fitting parameters in log-log scale.

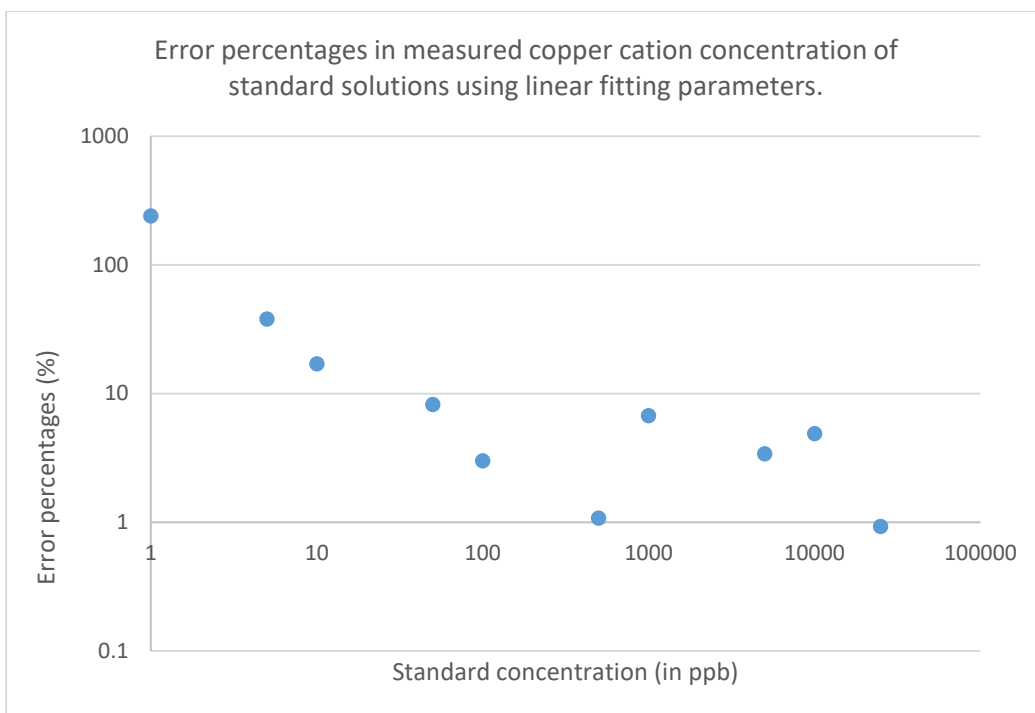


Figure 5.12 Error percentages in measured copper cation concentration of standard solutions using linear fitting parameters.

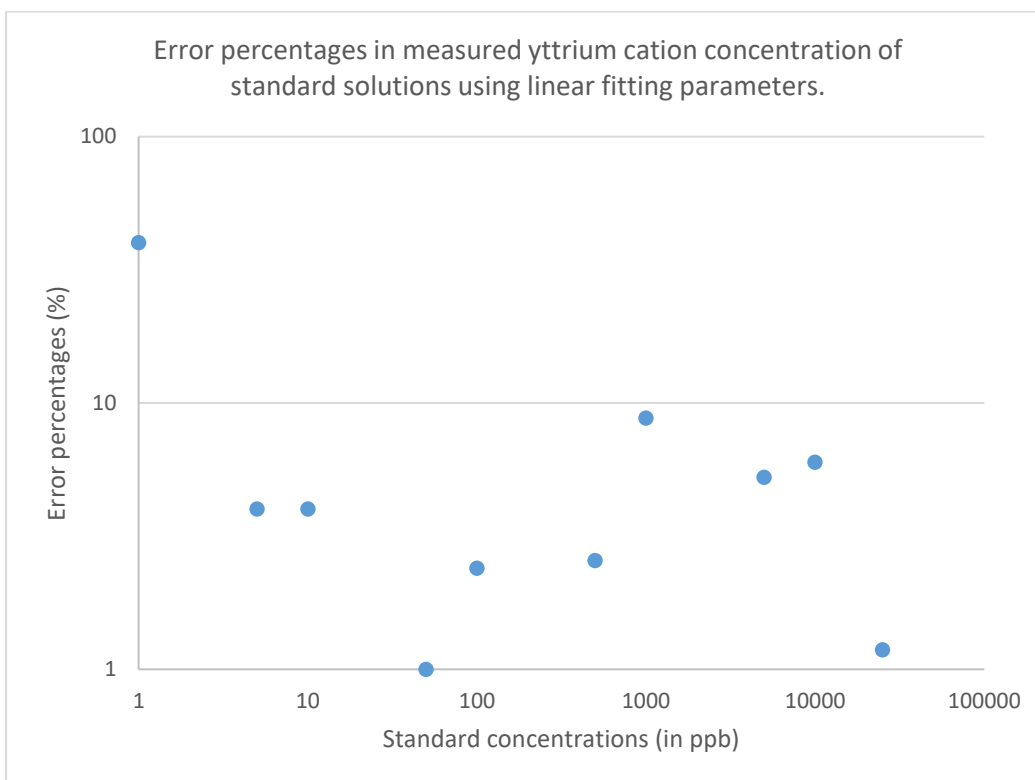


Figure 5.13 Error percentages in measured yttrium cation concentration of standard solutions using linear fitting parameters.

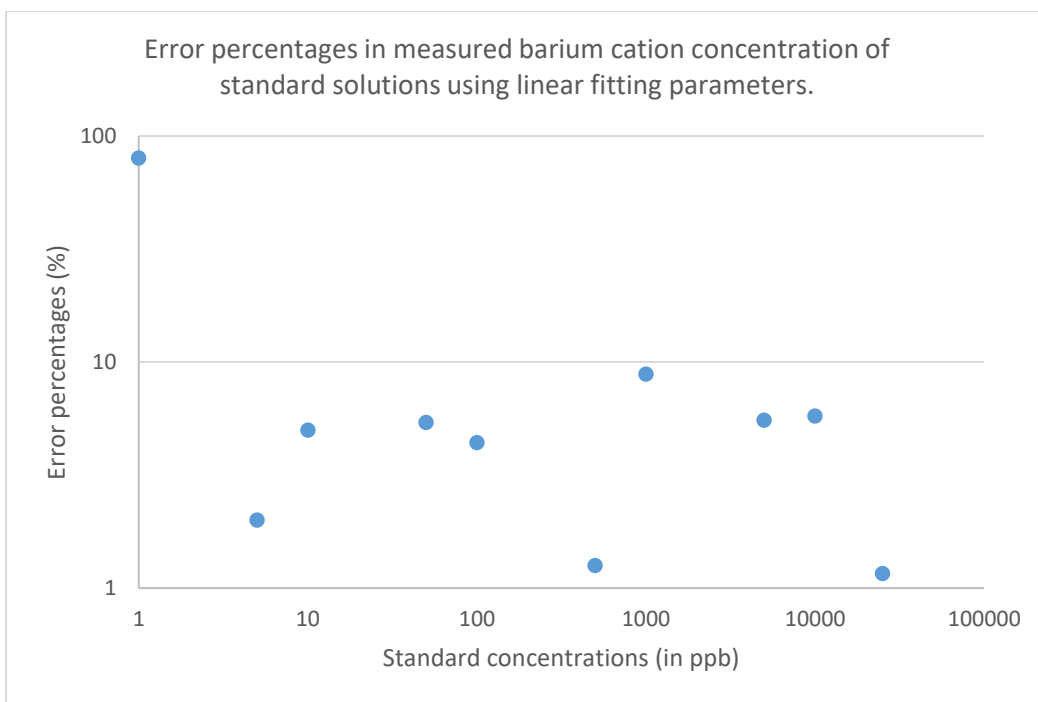


Figure 5.14 Error percentages in measured barium cation concentration of standard solutions using linear fitting parameters.

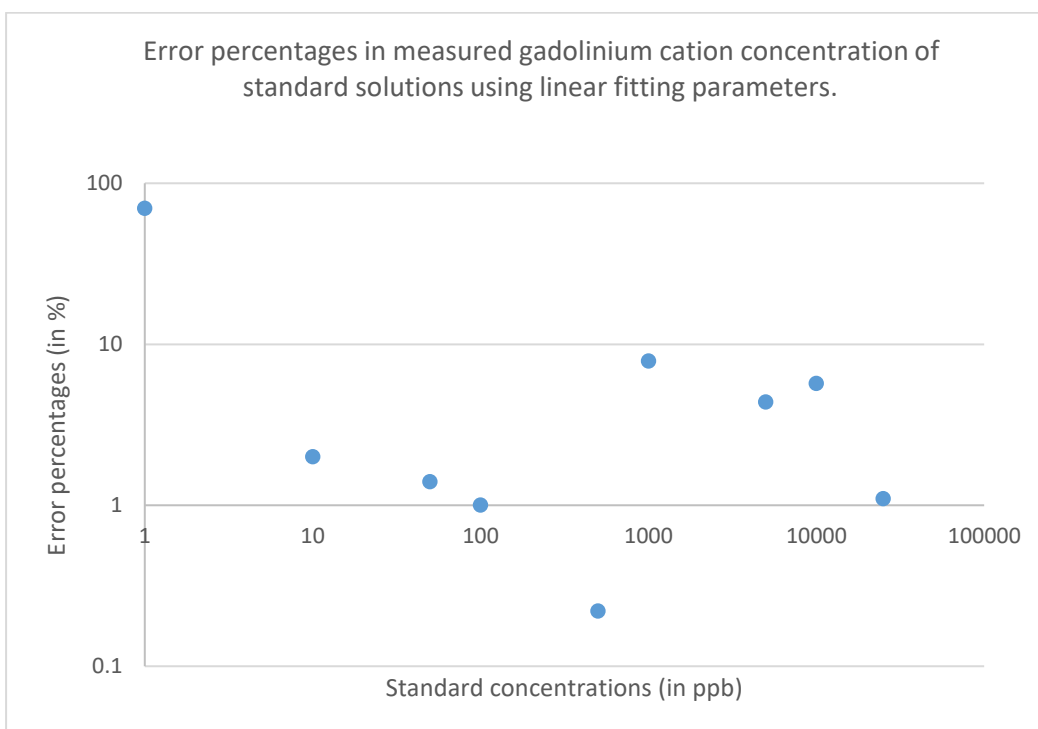


Figure 5.15 Error percentages in measured barium cation concentration of standard solutions using linear fitting parameters.

It is clear from Figures 5.12 through 5.15 that there is a decrease in the error percentage of the measured cation concentration with increasing standard concentrations in linear regression fitting mode. Table 5.15 shows the typical absolute concentration values (in

ppb) measured in the three reference samples with 50 mL of 2 percent nitric acid which is used as the standardized value of solvent quantity for all the samples.

Table 5.4 Measured absolute concentration values (in ppb) for the three reference samples dissolved in 50 mL of 2 percent nitric acid.

Sample ID	Cu	Y	Zr	Ba	Gd
M4 (1.5 μm thick)	3129.3	728.6	147.7	4015.7	1235.7
PM 206 3 (4.5 μm thick)	5067.7	1439.2	402.8	7657.5	2790.3
PM 206 4 (4.5 μm thick)	5996	1684.8	468.5	8965.4	3152.3

It can be seen from Table 5.4 that the typical measured values of copper from samples that vary in thickness from 1.5 μm to 4.5 μm lies within the range of 3000 – 6000 ppb in absolute concentration. So errors in the linear regression fit between 1000 ppb to 10000 ppb ranging from 6.4 percent to 3.8 percent respectively modulate the measured values in this range with errors depending upon where the actual point lies on the fit. The extremely high error found at 1 ppb for the copper cation in the standards does not affect the measurements in any manner (unless there are samples to be measured in this range). Tracing out the relevant intervals for all the cations reveals an error between 3 – 10 percent for the measured value of each cation. These errors tend to be additive in nature since when calculating normalized concentration, the relative concentration of each cation (obtained by dividing the absolute concentration values from the ICP MS in ppm by the atomic weight) is divided by the total concentration which is the sum of relative concentrations of all the cations. All of this leads to significant issues with reproducibility and repeatability of measurements and quality of correlations with physical and magnetic properties deteriorate substantially.

To address these issues, a fundamental paradigm shift was needed in the approach to the problem. The method of internal standardization, which has been described above, fundamentally relies on the method of regression fits to generate estimates of measured cation concentrations. But it should be pointed out that the raw signal (**as/bs** in Figure 5.2) is the actual ratio of the measured counts on the detector. This column is highlighted in Figure 5.16. This is purely the ratio of counts on the detector of the analyte signal i.e., cation of interest divided by the internal standard signal ^{115}In (istd). This ratio is the actual figure of interest that should be evaluated since the final concentration (x) that is measured is simply generated from the value on the y-axis (ratio) and plugging it into an equation that can output a value for the x-axis (absolute concentration) . As long as all other physical factors such as non-turbulence in the flow rate, temperature of the plasma, diameter of the cones etc. remain stable, this value should be repeatable and reproducible with remarkable accuracy. Table 5.5 lists out the values of this ratio for the three reference samples that were measured.

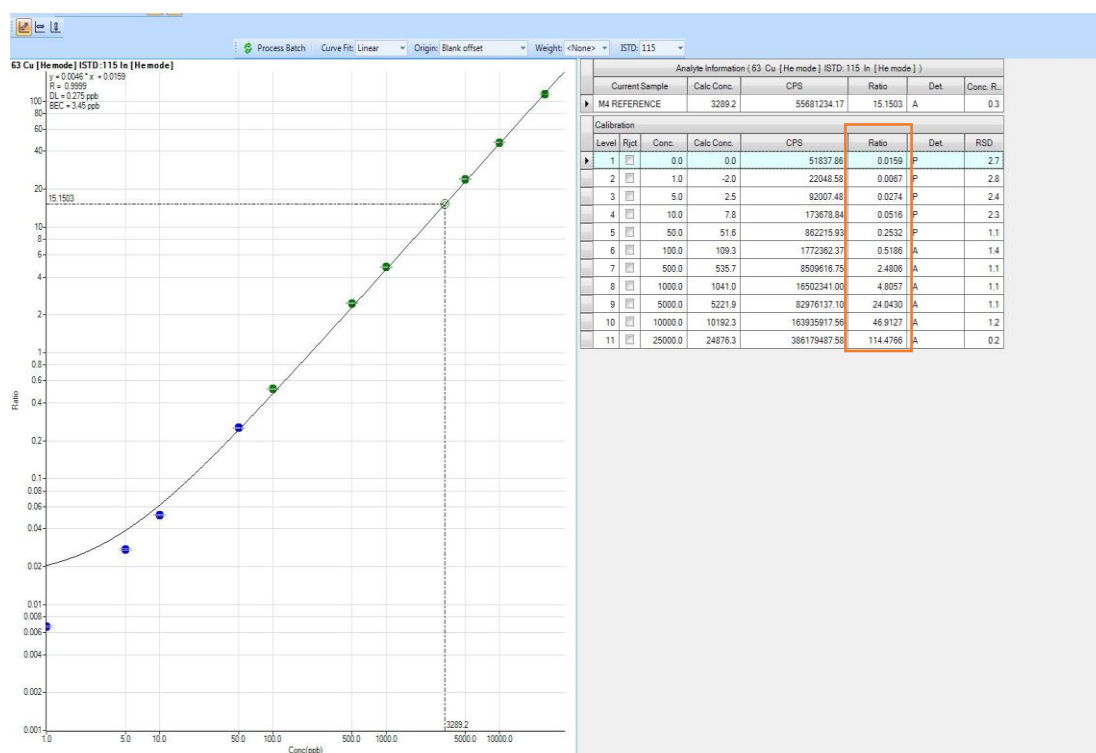


Figure 5.16 Linear fitting for the copper cation concentration in the standard solutions from 0 PPB to 25 PPM with highlighted column displaying (analyte/istd) count ratio.

Table 5.5 Ratio of (analyte/istd) counts for the three reference samples dissolved in 50 mL of 2 percent nitric acid.

Sample ID	Cu	Y	Zr	Ba	Gd
M4 (1.5 μm thick)	15.1503	5.3263	0.4067	6.5694	6.8173
PM 206 3(4.5 μm thick)	24.3614	10.4608	1.2925	12.2890	14.8754
PM 206 4(4.5 μm thick)	28.7027	12.2359	1.5592	14.2879	17.2958

It can clearly be seen from Table 5.5 that when considering values of standard concentrations for measuring copper cation concentration, only those standards that lie in the range of (analyte/istd) ratios 20 to 50 need to be considered. Referring back to the highlighted column in Figure 5.16, it can be seen that fitting a curve or a line through the standards ranging from 500 to 5000 is sufficient to cover this entire range of measurements (4.61 – 44.10 in analyte/istd ratio). Fitting a higher order polynomial like a quadratic regression equation that can provide an exact solution to these three points gets rid of the errors found earlier with linear regression fit. Figure 5.17 is an example of the fitting of the copper cation concentrations with a quadratic regression fit.

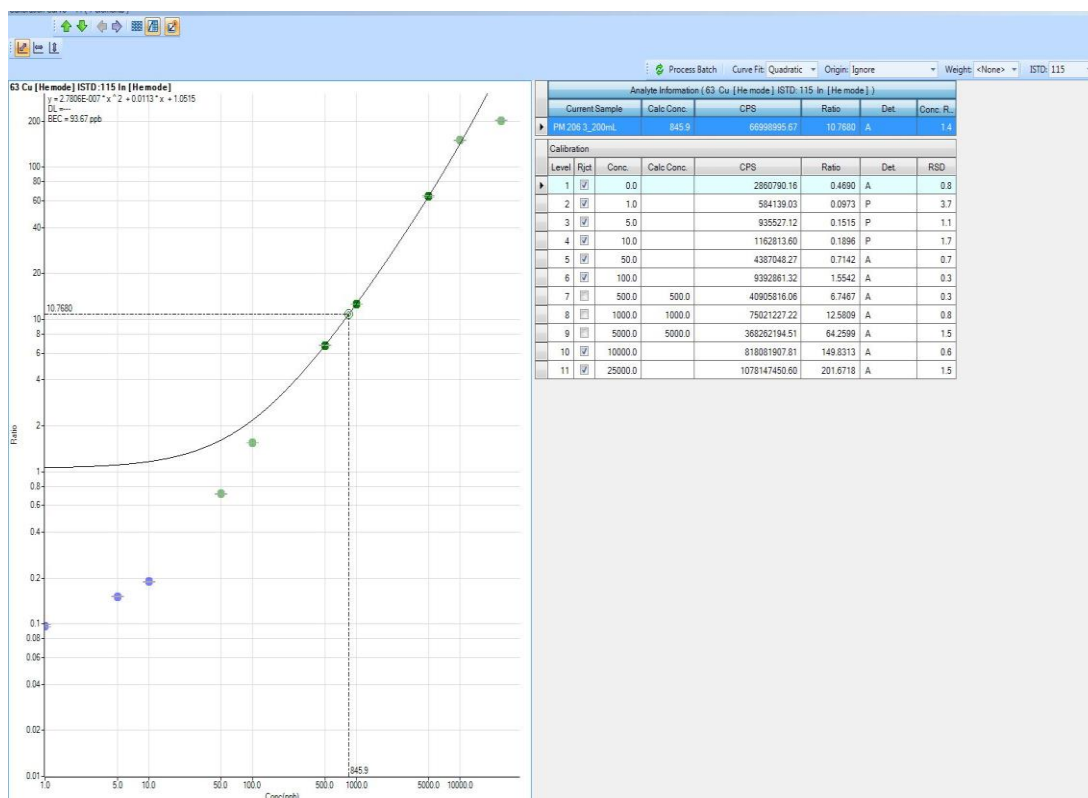


Figure 5.17 Quadratic fitting for copper cation concentration in the standard solutions from 500 ppb to 5 ppm.

Ignoring the points at higher and lower ratios of (istd/analyte) counts gives three pairs of (x,y) through which a quadratic equation of the form $y = ax^2 + bx + c$ (three variables, three equations) can almost always be fitted exactly unless they are completely non-collinear. It should be pointed out that despite getting rid of the basic calibration errors in the standard solutions, the values that are obtained still need to be checked for consistency, physical meaning and relevancy. It should also be pointed out that this experiment was strictly carried out keeping the amount of solvent constant at 50 mL with the thickness range of the samples between 1.5 – 4.0 μm . All the samples that are being currently fabricated using the AMOCVD lie within this range so this method is well validated for the current set of applications. For thinner or thicker samples, it is recommended to vary the amount of solvent accordingly to bring the concentration levels within the validated range since going outside this range can vary the slope of the fitting which will undermine the accuracy of the fitting as shall be seen in the case of zirconium.

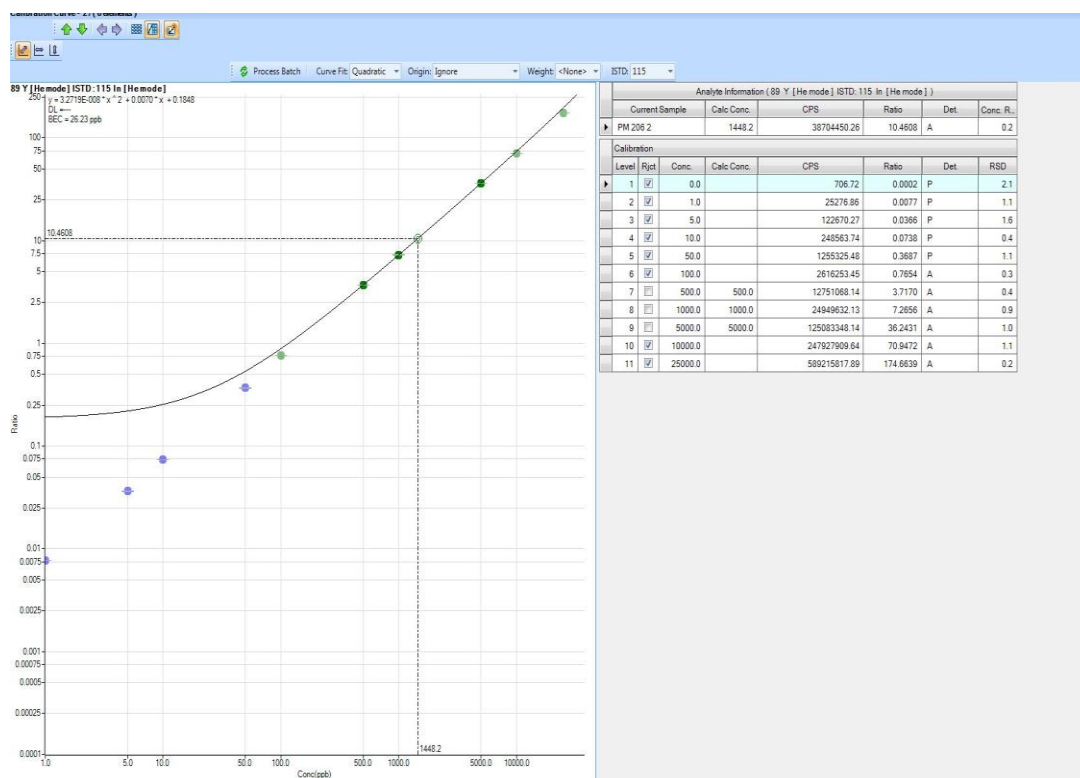


Figure 5.18 Quadratic fitting for yttrium cation concentration in the standard solutions from 500 ppb to 5 ppm.

Figure 5.18 displays the fitting for yttrium cation concentration measurements where the signal ratio of analyte to istd lies in the range of 5 to 13 and the curves are fitted from 500 ppb to 5 ppm accordingly.

Figure 5.19 displays the fitting for barium where the analyte to istd signal ratio lies in the range of 6 to 15 and the curves are fitted from 1 ppm to 10 ppm accordingly.

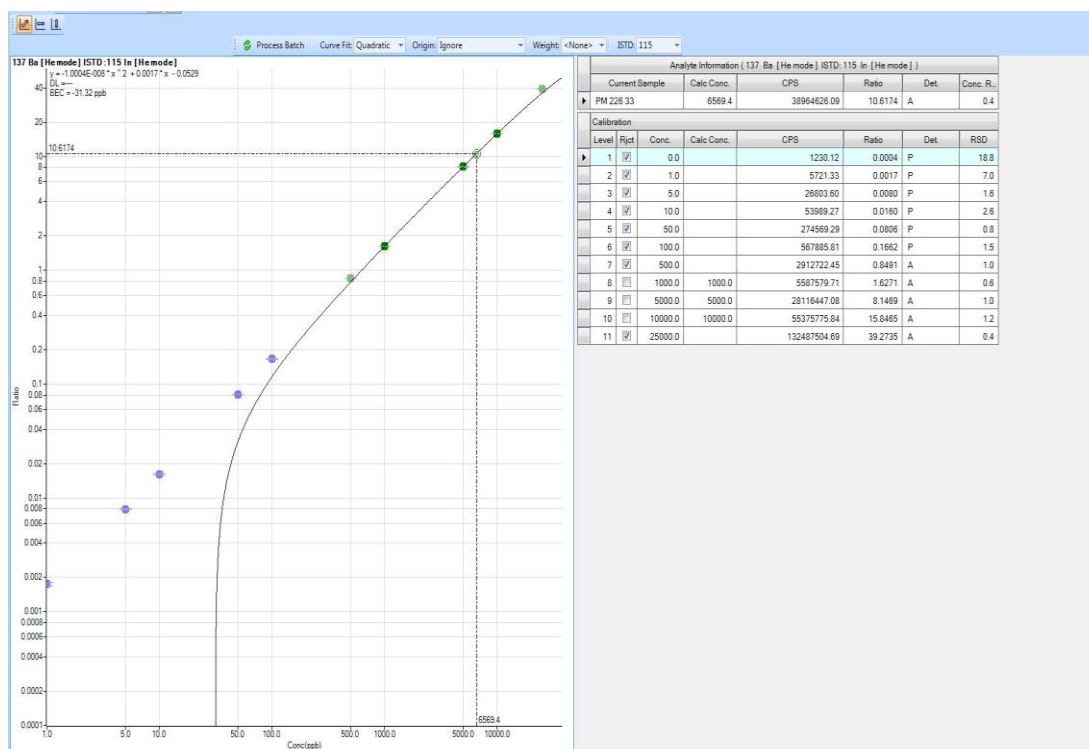


Figure 5.19 Quadratic fitting for barium cation concentration in the standard solutions from 1 ppm to 10 ppm.

Figure 5.20 displays the fitting for gadolinium where the analyte to istd signal ratio lies in the range of 6 to 18 and the curves are fitted from 500 ppb to 5 ppm concentration accordingly. Figure 5.18 – 5.20 essentially show that the variations in the interval of the fitting required for each individual precursor molecule are dictated by the stoichiometry of the REBCO thin film that is being analyzed i.e., nominal $(\text{RE})_{1.2}\text{Ba}_2\text{Cu}_3$ contains nearly twice the amount of barium as rare earth and thrice the amount of copper so the fitting intervals are adjusted accordingly. Zirconium, being a dopant, is nominally present in the 50 – 500 ppb range.

Figure 5.18 – 5.20 essentially show that the variations in the interval of the fitting required for each individual precursor molecule are dictated by the stoichiometry of the REBCO thin film that is being analyzed i.e., nominal $(\text{RE})_{1.2}\text{Ba}_2\text{Cu}_3$ contains nearly twice the amount of barium as rare earth and thrice the amount of copper so the fitting intervals are adjusted accordingly. Zirconium, being a dopant, is nominally present in the 50 – 500 ppb range.

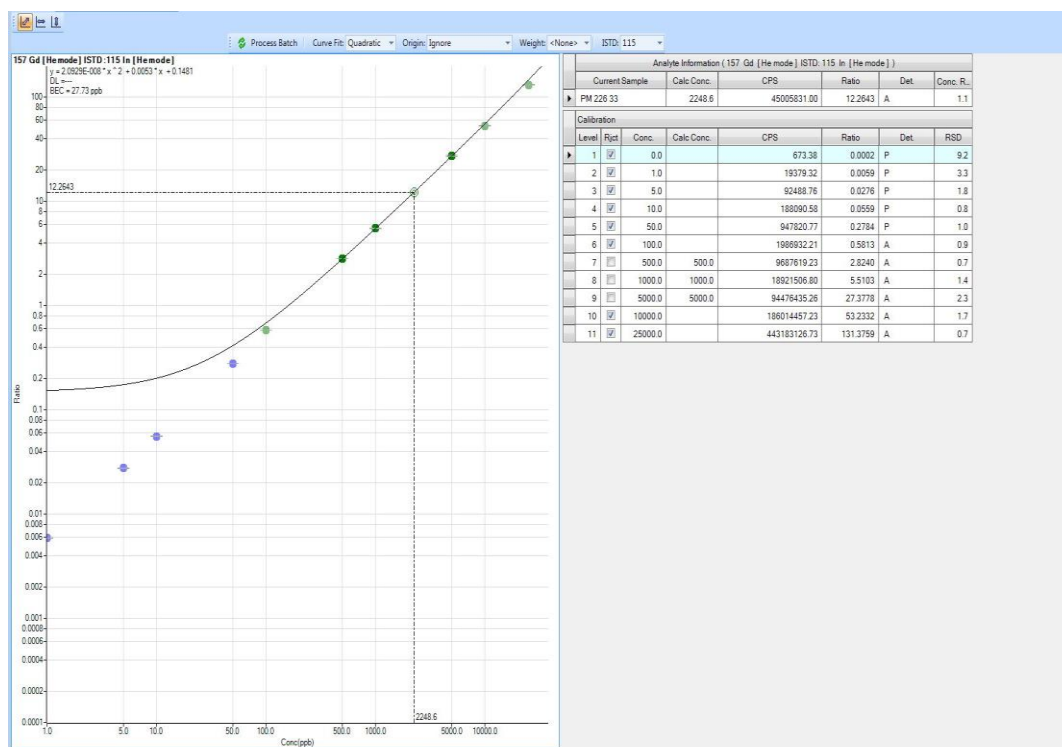


Figure 5.20 Quadratic fitting for gadolinium cation concentration in the standard solutions from 500 ppb to 5 ppm.

Zirconium is fitted in the range of 0 – 500 ppb with a quadratic running through all the standard concentration points in the interval with minimal errors in the fit in Figure 5.21. However, the curve is found to be quite nonlinear below 10 ppb where the measurements become unreliable. Instrumental detector response should be linear and there is no evidence that it has to behave in a non-linear fashion for the case of zirconium alone below a certain concentration. This is purely an artifact of the zirconium standards behaving in a nonlinear fashion upon dilution.

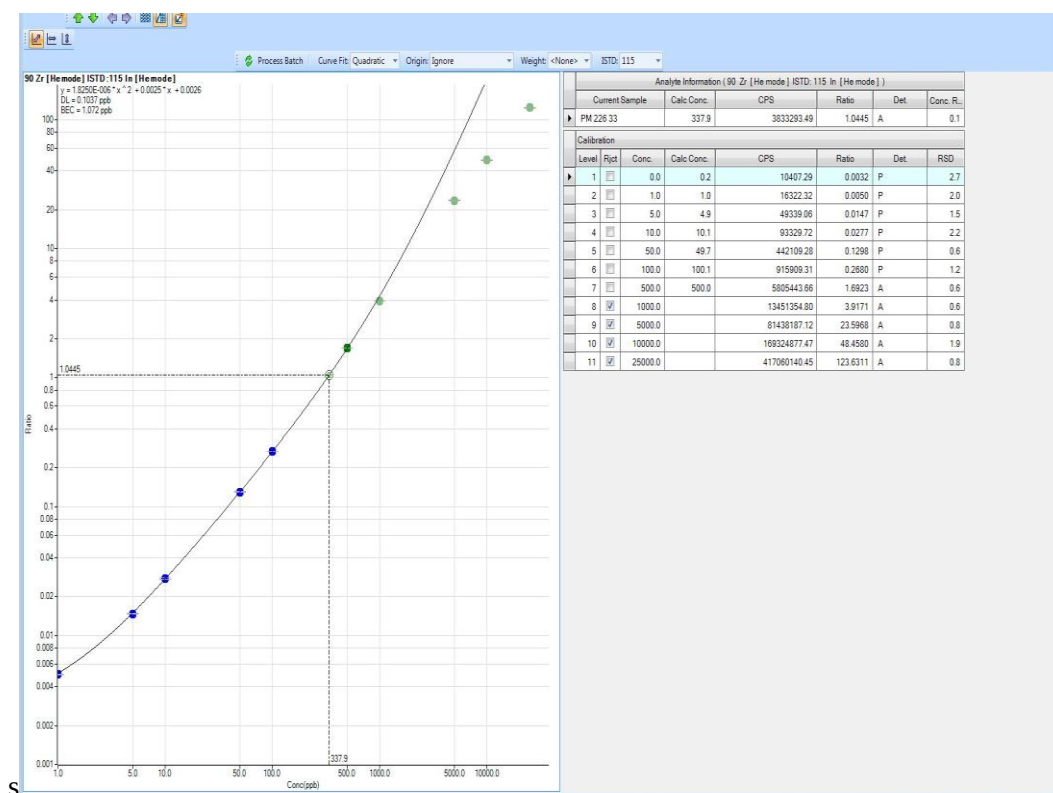


Figure 5.21 Quadratic fitting for zirconium cation concentration in the standard solutions from 0 ppb to 500 ppb.

Table 5.6 displays the final normalized atomic concentration in percentage values upon using all the absolute concentration values that are obtained from the fitting procedure

Table 5.6 Normalized concentration percentages of cation atomic concentration (in %) for the three reference samples dissolved in 50 mL of 2 percent nitric acid.

Sample ID	Cu	Y	Zr	Ba	Gd
M4 (1.5 μm thick)	51.2	8.5	1.7	30.4	8.2
PM 206 3(4.5 μm thick)	46.0	9.3	2.5	32.2	9.9
PM 206 4(4.5 μm thick)	46.3	9.3	2.5	32.0	9.8

But the Zr composition of these three samples, which are being used as references, are well known from experience with the older set of standards and they are expected to have 0.9, 1.5 and 1.5 atomic concentration percentage respectively. Figure 5.22 shows the disparity

in the values that are obtained from the measurement and the actual cation concentration in a log-log plot.

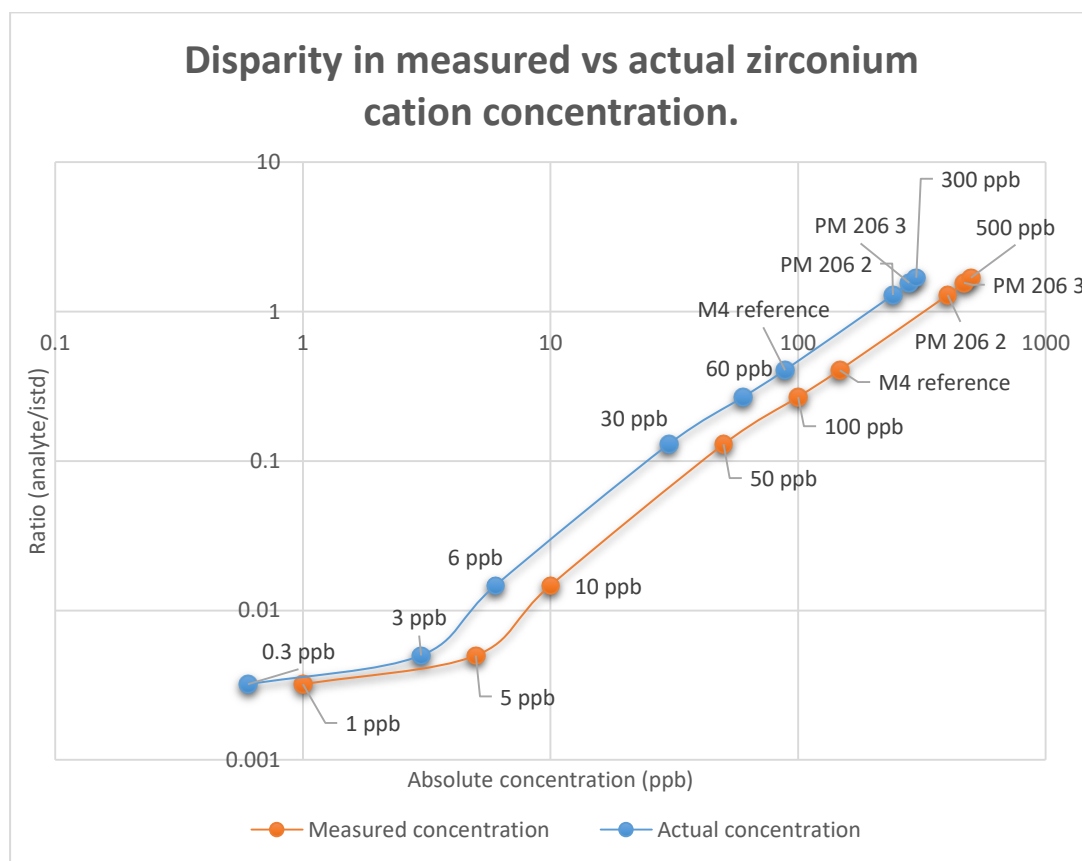


Figure 5.22 Disparity between measured concentration and actual concentration of zirconium in the three reference samples dissolved in 50 mL of 2 percent nitric acid.

It is found that the measured cation concentration for the zirconium is 1.66 times higher than the nominal values. So the measured values of the zirconium cation concentrations are all multiplied with a correction factor of 0.6 to bring the measured values within the range of nominal values. All the samples that lie in this range also get automatically corrected. Figure 5.22 clearly displays the linear region of the log-log graph extends down to about 10 ppb in measured concentration curve below which it becomes sharply nonlinear. The disparity exists because of differences in the measured calibration values and the actual concentration values due to the curve fitting procedure in the current set

of standards. Upon applying the correction factor, Table 5.6 shows the corrected measured values reaching a good agreement with the nominal values.

Table 5.6 Corrected normalized concentration percentages of cation concentration (in %) for the three reference samples dissolved in 50 mL of 2 percent nitric acid.

Sample ID	Cu	Y	Zr	Ba	Gd
M4 (1.5 μm thick)	51.6	8.6	1.0	30.6	8.2
PM 206 3(4.5 μm thick)	46.5	9.4	1.5	32.5	10.0
PM 206 4(4.5 μm thick)	46.8	9.4	1.5	32.4	9.9

5.1.2. Continuous Calibration Verification (CCV) and Statistical Quality Control (SQC)

The aforementioned techniques that have been developed in Section 5.1.1 have been implemented successfully for the measurements carried out regularly with the ICP MS. The three reference samples are used at the start, in the middle and at the end of the run to check for drift, repeatability and reproducibility of measurements and the same analytical techniques of curve fitting is applied to all the samples. This technique is known as Continuous Calibration Verification (CCV) and gives assurance to the quality of measurements. Any significant deviation in the values obtained on the reference samples immediately highlights an issue with the instrument and corrective actions are initiated to bring the measurements back to nominal levels. Significant amounts of data on these samples have also been collected and time-scatter plots have been implemented to track the variation in their values over time. Preventative as well as reactive maintenance are tracked through these plots and Statistical Quality Control (SQC) of the instrument has been implemented in this fashion.

Table 5.7 displays the output of a typical measurement performed using the ICP MS.

Table 5.7 Corrected normalized concentration percentages of cation concentration (in %) for a typical run in the ICP MS with the three reference samples highlighted.

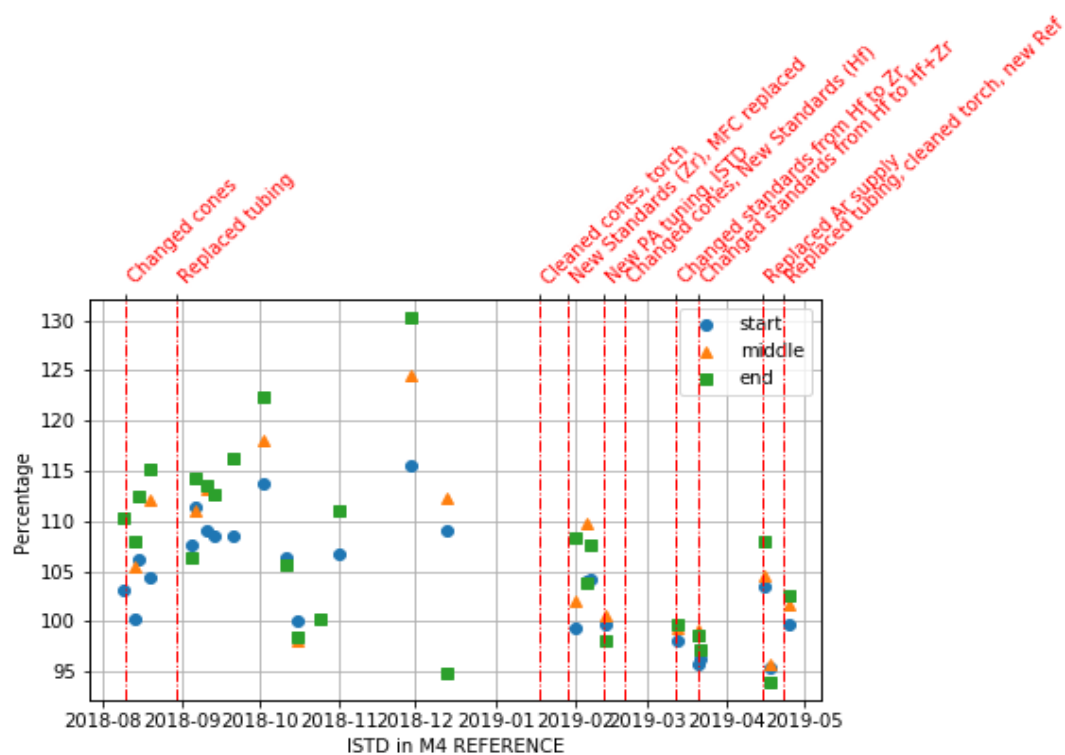
Sample	Normalized Concentration %				
	Cu	Y	Zr	Ba	Gd
M4 REFERENCE - S	51.2	8.7	1.0	30.9	8.1
PM 206 2 - S	46.6	9.7	1.4	32.2	10.1
PM 206 3 - S	46.5	9.7	1.5	32.2	10.1
221 2	46.8	11.1	0.5	30.7	10.9
221 3	46.4	11.2	0.4	31.1	10.9
221 4	46.2	11.8	0.6	30.0	11.4
221 5	46.7	11.5	0.4	30.4	11.0
221 6	46.8	11.1	0.4	30.9	10.7
221 7	46.5	11.3	0.5	31.0	10.8
221 8	47.3	10.9	0.4	30.8	10.6
221 9	46.7	11.1	0.4	31.0	10.8
221 10	46.6	11.5	0.5	30.5	10.8
221 11	45.7	13.1	0.8	28.5	11.9
221 12	45.9	11.9	0.6	30.7	10.9
221 13	45.9	11.6	0.7	31.1	10.7
221 14	45.1	11.7	1.6	30.3	11.2
221 15	45.5	10.8	1.1	32.3	10.4
221 16	45.9	10.7	1.0	32.0	10.4
221 17	43.7	11.4	1.7	32.8	10.4
221 18	44.8	11.6	1.3	31.2	11.2
221 19	44.8	11.7	1.2	31.2	11.2
221 20	44.4	11.9	1.2	31.1	11.5
221 21	44.1	10.6	1.4	33.7	10.2
221 22	44.0	10.4	1.3	34.2	10.1
221 23	44.7	10.4	1.1	33.9	9.9
221 24	41.4	11.3	1.8	35.4	10.2
M4 REFERENCE - M	51.8	8.7	0.9	30.7	7.9
PM 206 2 - M	47.1	9.8	1.4	31.7	9.9
PM 206 3 - M	47.0	9.8	1.5	31.9	9.8
221 25	45.3	11.0	0.7	32.5	10.5
221 26	44.9	11.0	0.5	33.0	10.6
221 27	44.8	10.8	0.5	33.5	10.4
221 28	45.2	10.6	0.5	33.6	10.2
221 29	44.2	11.2	0.7	33.4	10.7
221 30	44.5	10.5	0.5	34.3	10.2
221 31	44.5	10.5	0.5	34.4	10.1
221 32	44.0	10.7	0.6	34.4	10.2
221 33	44.4	10.4	0.6	34.7	10.0
234 1A	48.1	10.9	0.4	29.9	10.7
234 2A	47.7	10.4	0.4	31.2	10.4
234 3A	47.6	10.3	0.3	31.6	10.2
234 4A	47.7	10.4	0.3	31.3	10.3
234 7A	47.5	10.7	0.4	30.8	10.6

(Table 5.7 continued)

234 8A	43.6	12.5	0.7	32.1	11.1
234 9A	44.0	12.6	0.3	31.9	11.3
234 10A	43.9	12.3	2.1	30.7	11.0
234 11A	42.5	12.2	1.1	33.2	11.1
234 12A	42.3	12.2	1.0	33.3	11.1
234 13A	42.3	12.3	0.8	33.3	11.3
234 14A	42.4	11.9	1.1	33.7	10.9
234 15A	41.0	13.5	0.2	33.3	12.0
234 8B	42.0	13.4	0.6	32.4	11.6
234 9B	42.1	13.8	0.1	31.5	12.5
234 10B	42.0	13.3	0.6	32.3	11.7
234 11B	43.4	12.5	0.8	32.4	10.9
234 12B	43.4	12.4	0.8	32.3	11.0
234 13B	43.4	12.5	0.7	32.5	10.9
234 14B	43.1	12.4	1.0	32.9	10.7
234 15B	39.1	14.9	0.1	33.3	12.6
218 2	46.6	10.6	1.4	31.3	10.1
218 3	46.6	10.5	1.6	31.3	10.0
218 4	42.1	14.0	0.0	31.6	12.4
218 5	46.8	10.7	1.5	30.9	10.1
218 6	46.4	10.6	1.6	31.2	10.1
218 8	46.9	10.6	1.6	30.9	10.0
218 9	46.8	10.8	1.7	30.7	10.1
M4 REFERENCE – E	52.3	8.7	0.9	30.3	7.8
PM 206 2 – E	47.1	9.9	1.4	31.8	9.8
PM 206 3 – E	47.0	9.8	1.5	31.9	9.8

The data for the references are extracted from all the measurements and are plotted on a six-sigma time-scatter plot from Figures 5.23 – 5.39. The plots also act as a maintenance log and timestamps for preventative maintenance scheduling as well as any repairs/modifications carried out in the instrument and act as a quality check. For example, the plots have proved to be instrumental in addressing internal standard drift that was observed climbing up steadily from 11/2018 to 12/2018 in Figure 5.25, so the ISTD peristaltic pump regulator nut was replaced in order to bring it back to nominal values in 01/2019. Performing extensive maintenance in the form of cone and torch cleaning leads to a completely clear line albeit displaying a seasoning time in Figure 5.23 to Figure 5.39 where the compositional values of the references that are measured take about two runs before stabilizing back to nominal values. All of these characteristics have been observed and plotted which adds to the depth of knowledge of instrument operation and control. Changing vendors or preparing new standard

solutions is another important event in the timeline of operation of the instrument since unreliable standards can cause the nominal values of the references to go out of bounds. If any unacceptable results are generated, corrective actions can immediately be taken by referring back to the log on the timeline



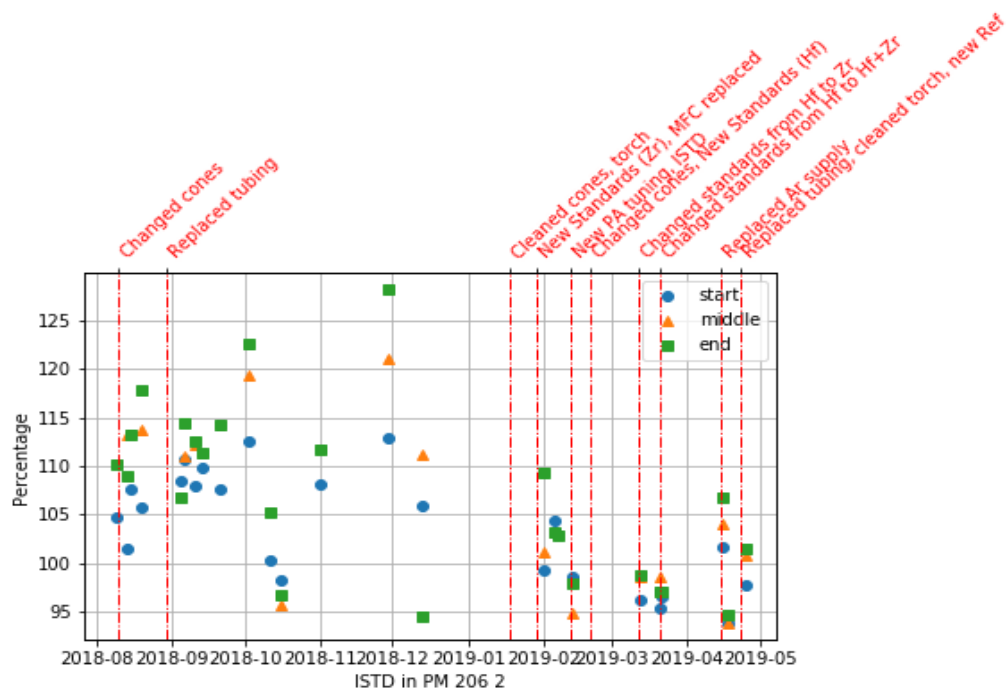


Figure 5.24 Time-scatter plot of ISTD variations over time of PM 206 2 sample at start, middle and end of the run.

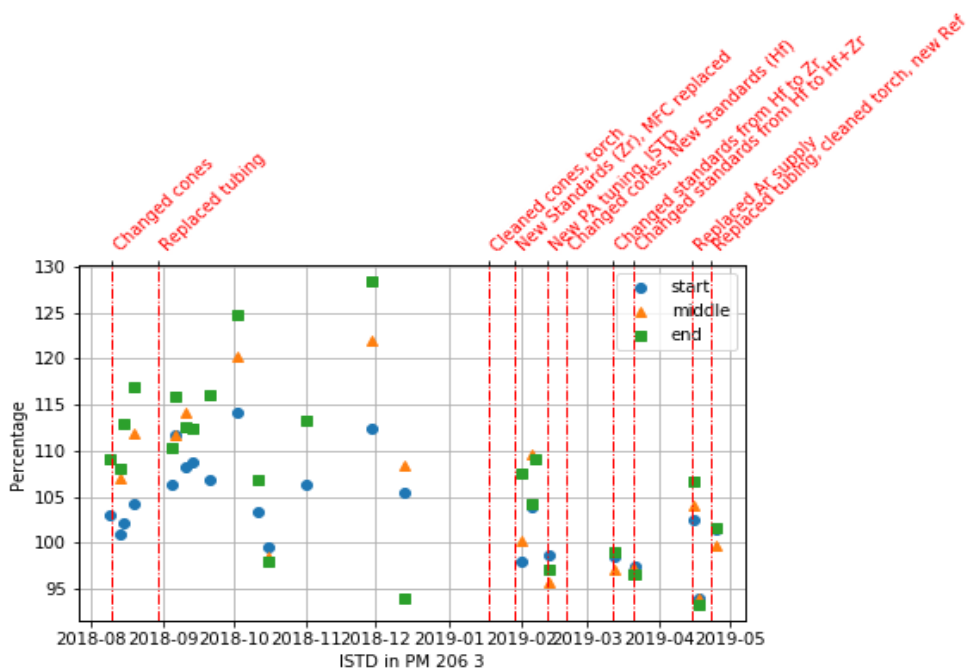


Figure 5.25 Time-scatter plot of ISTD variations over time of PM 206-3 sample at start, middle and end of the run.

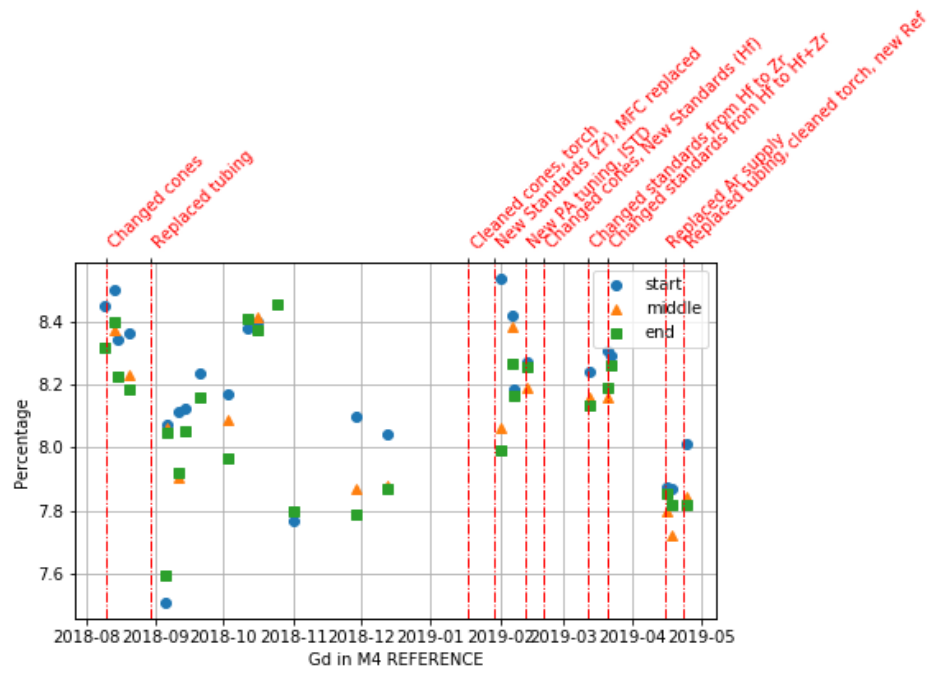


Figure 5.26 Time-scatter plot of Gd cation concentration variations over time of M4 sample at start, middle and end of the run.

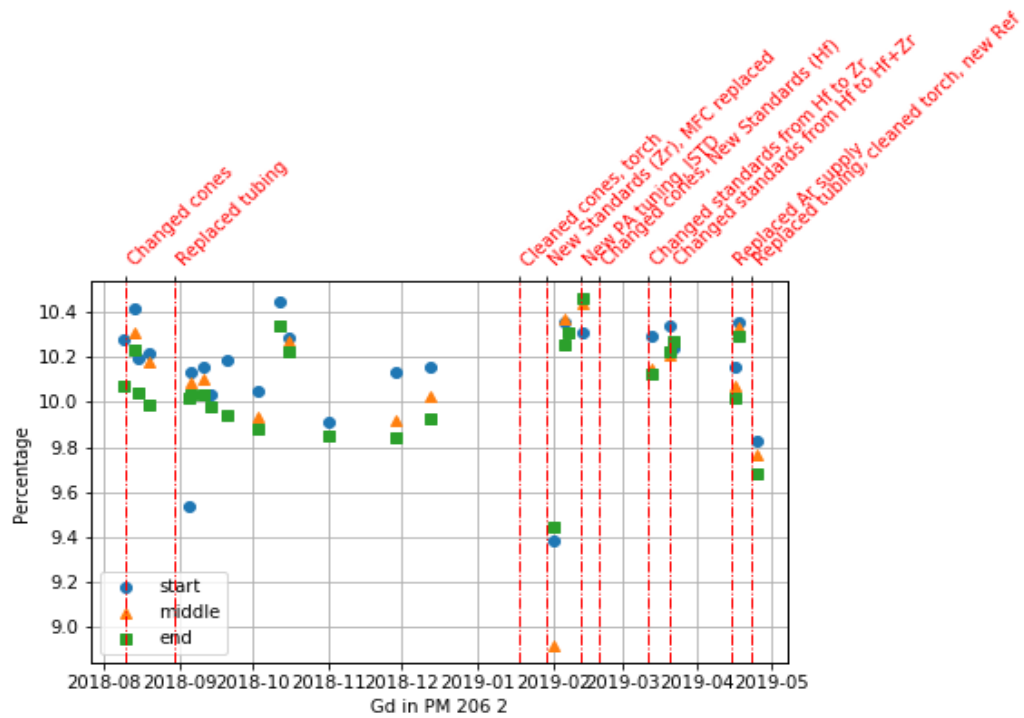


Figure 5.27 Time-scatter plot of Gd cation concentration variations over time of PM 206-2 sample at start, middle and end of the run.

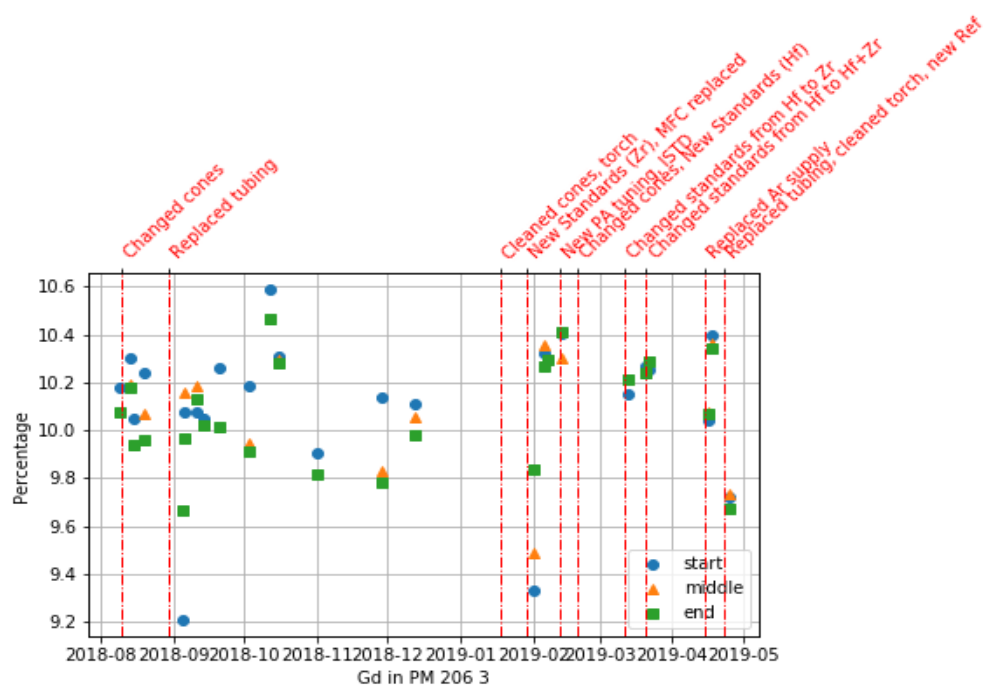


Figure 5.28 Time-scatter plot of Gd cation concentration variations over time of PM 206-3 sample at start, middle and end of the run.

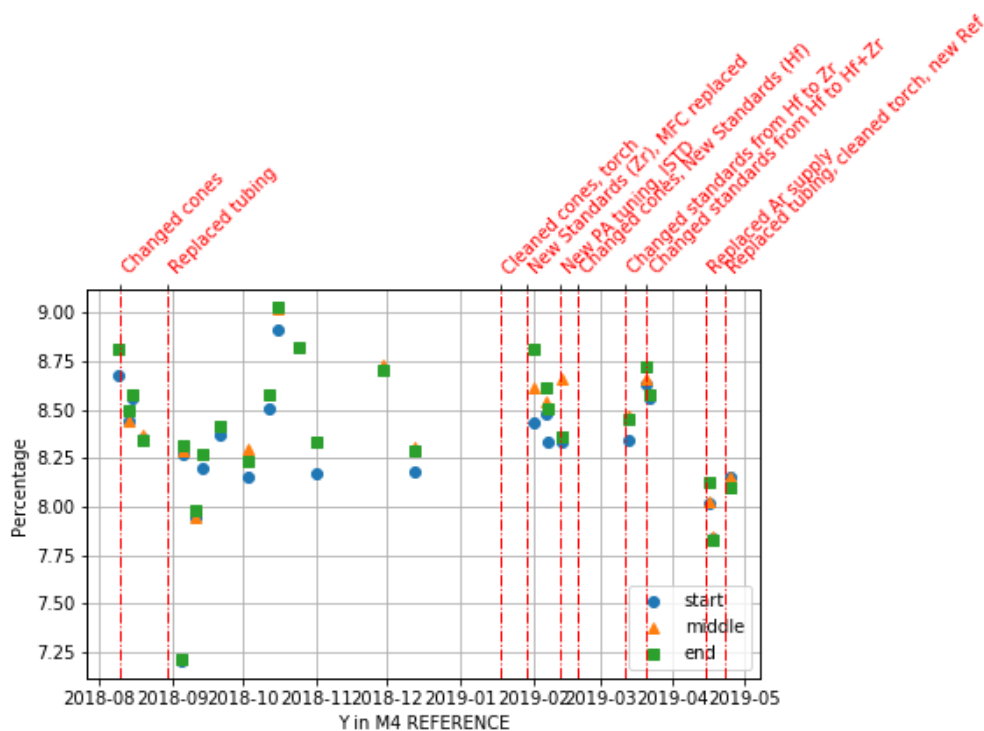


Figure 5.29 Time-scatter plot of Y cation concentration variations over time of M4 sample at start, middle and end of the run.

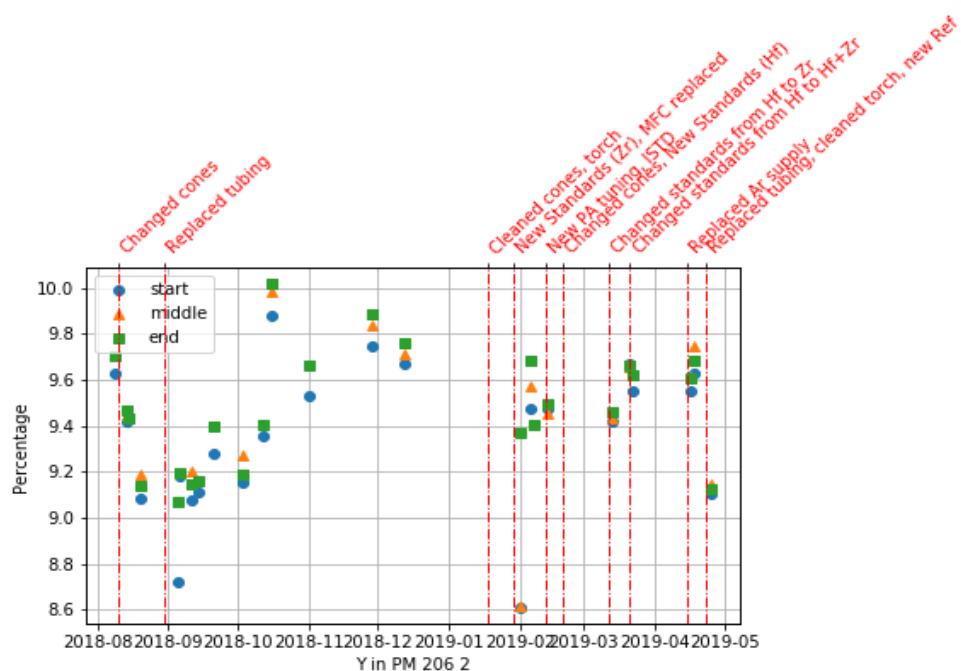


Figure 5.30 Time-scatter plot of Y cation concentration variations over time of PM 206-2 sample at start, middle and end of the run.

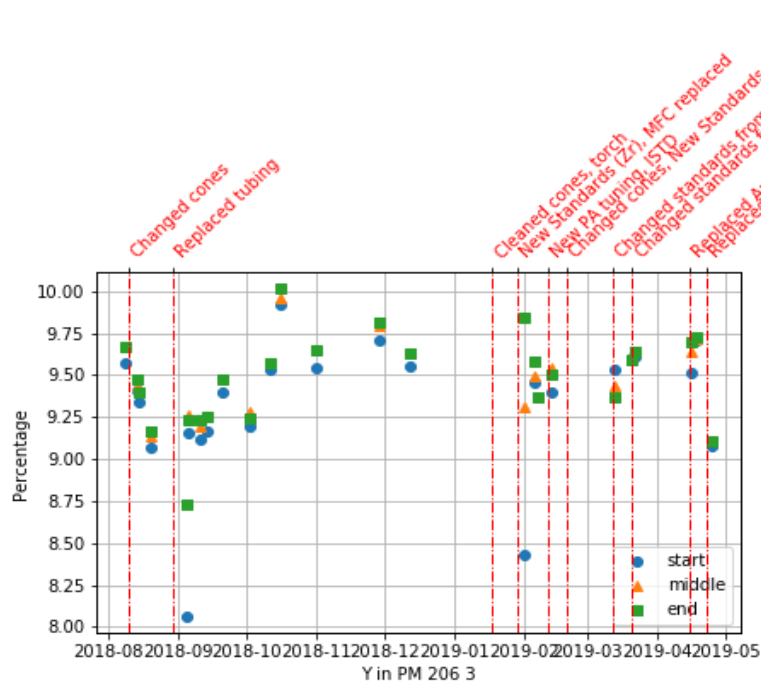


Figure 5.31 Time-scatter plot of Y cation concentration variations over time of PM 206-3 sample at start, middle and end of the run.

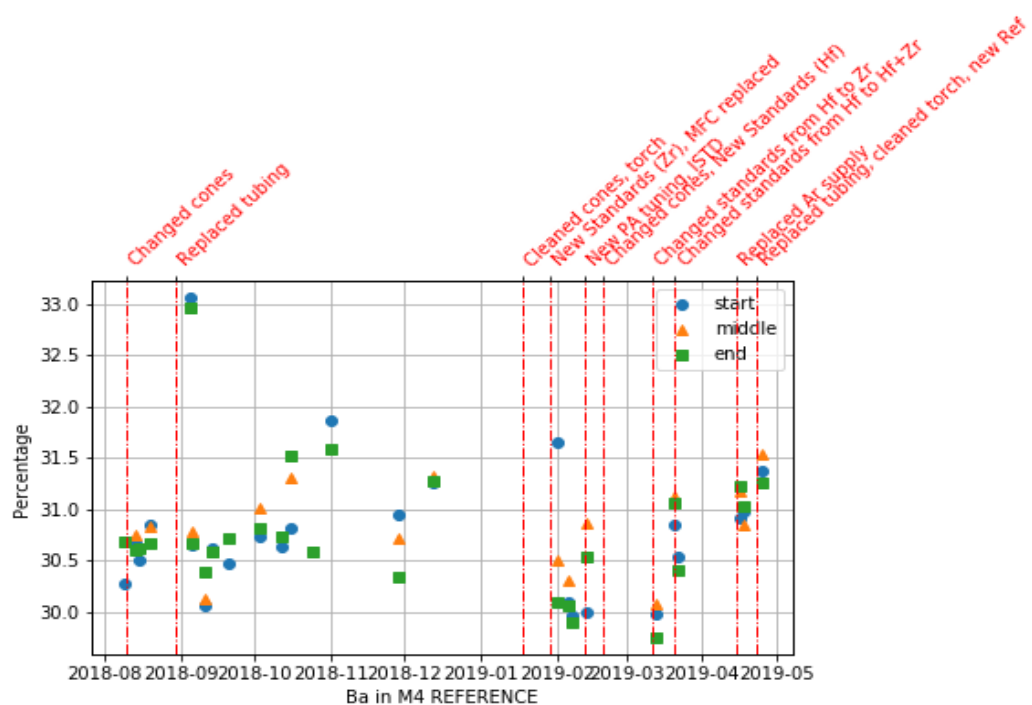


Figure 5.32 Time-scatter plot of Ba cation concentration variations over time of M4 sample at start, middle and end of the run.

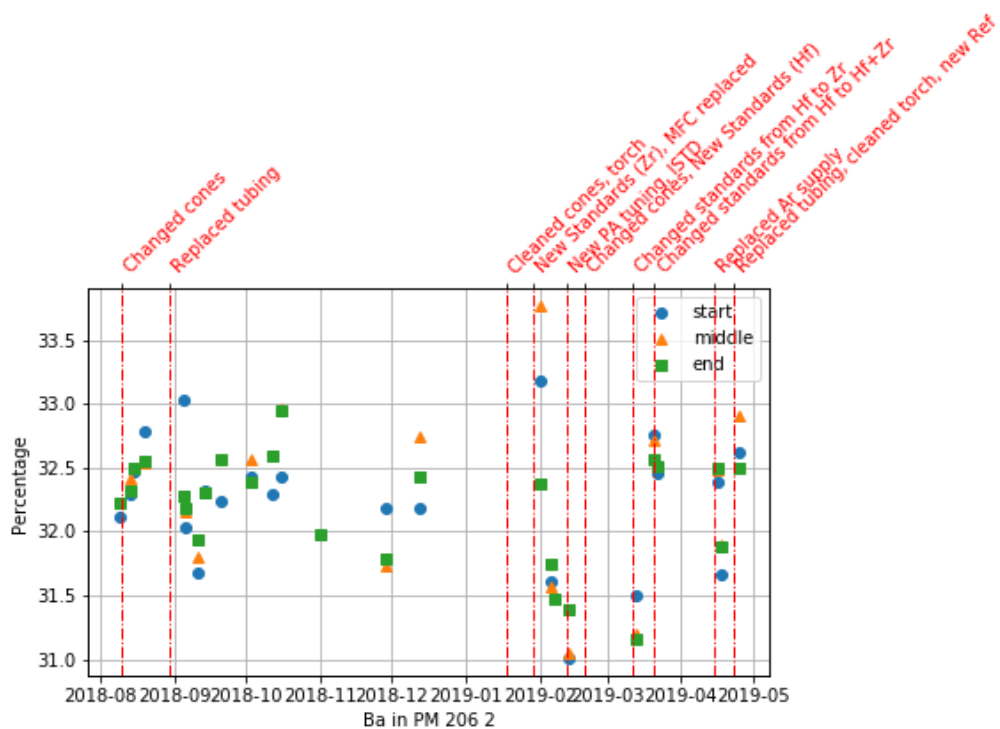


Figure 5.33 Time-scatter plot of Ba cation concentration variations over time of PM 206-2 sample at start, middle and end of the run.

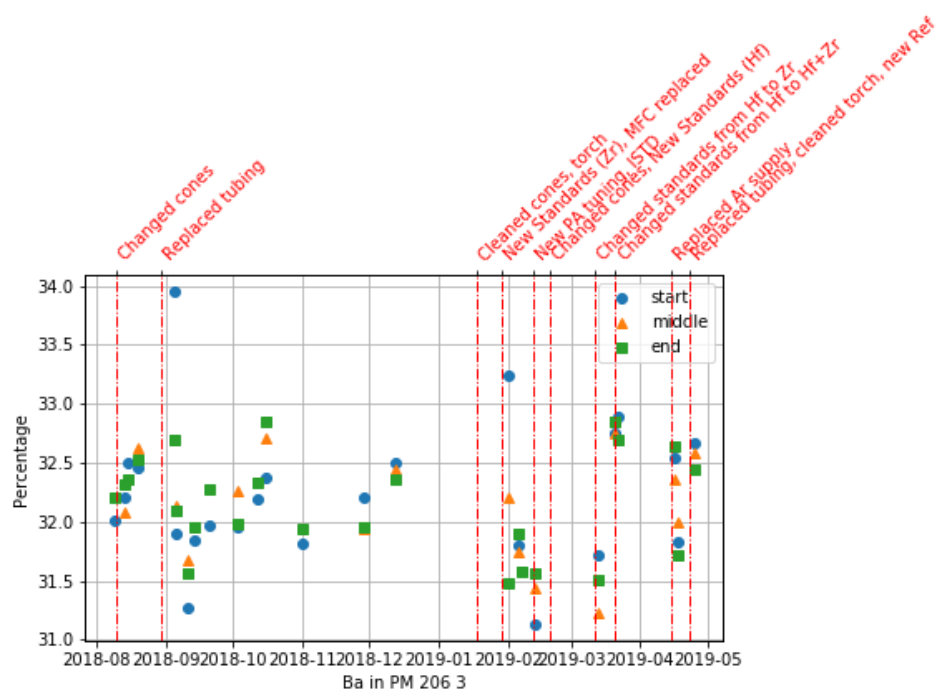


Figure 5.34 Time-scatter plot of Ba cation concentration variations over time of PM 206-3 sample at start, middle and end of the run.

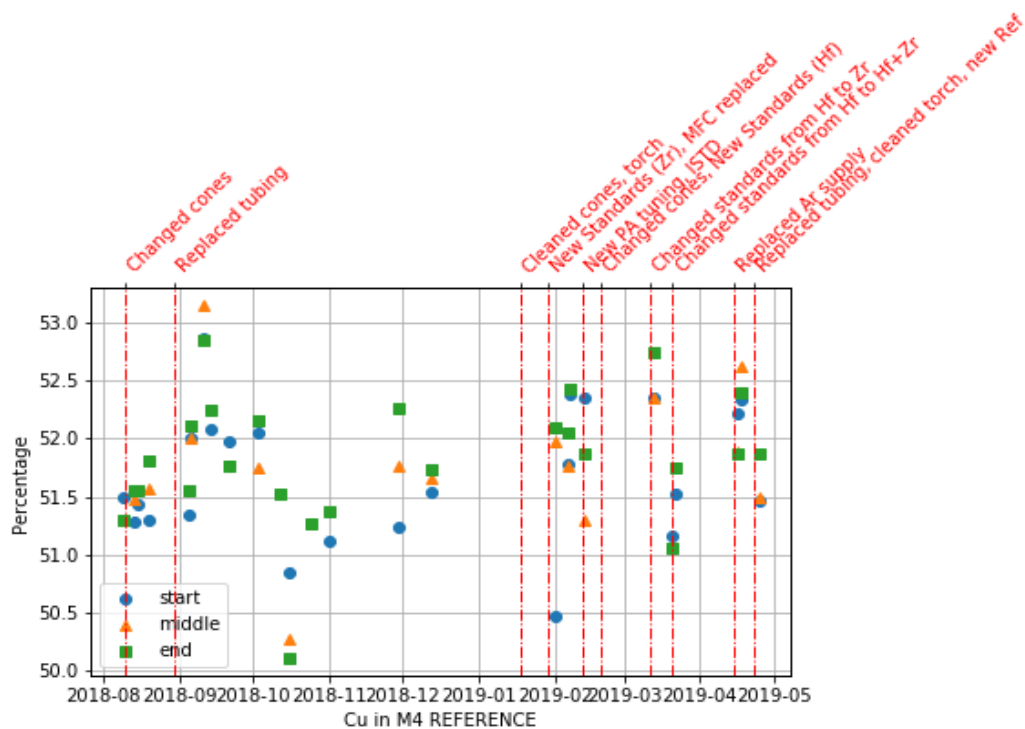


Figure 5.35 Time-scatter plot of Cu cation concentration variations over time of M4 reference sample at start, middle and end of the run.

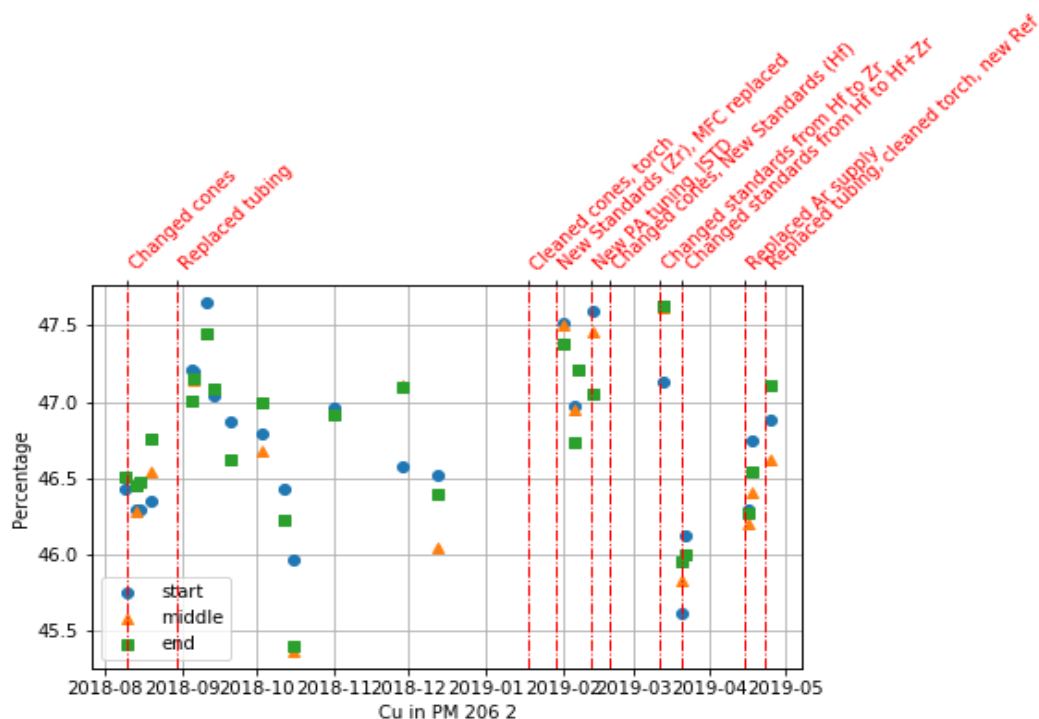


Figure 5.36 Time-scatter plot of Cu cation concentration variations over time of PM 206-2 sample at start, middle and end of the run.

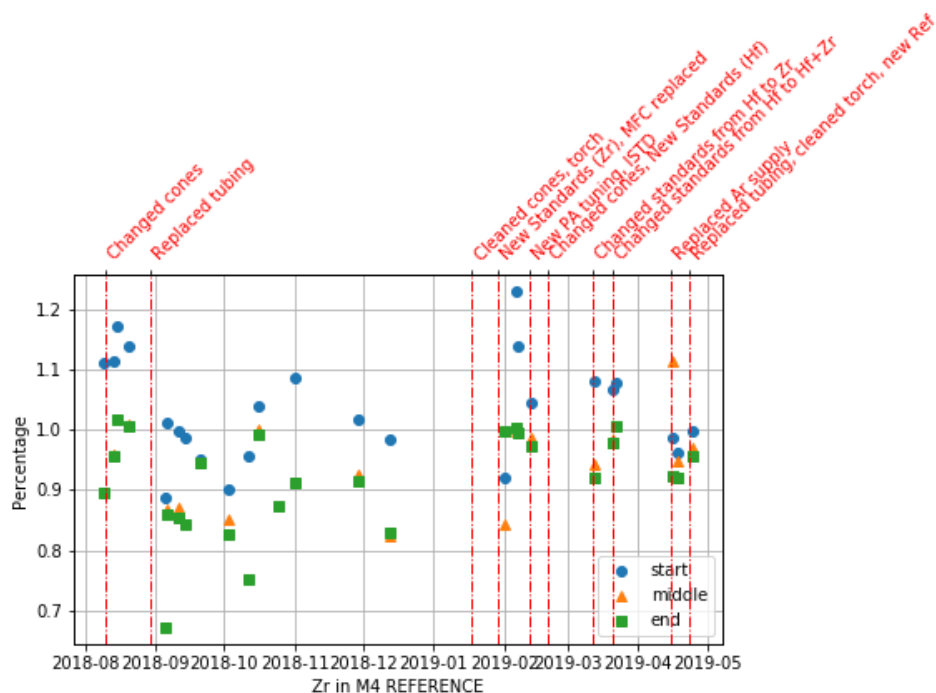


Figure 5.37 Time-scatter plot of Zr cation concentration variations over time of M4 sample at start, middle and end of the run.

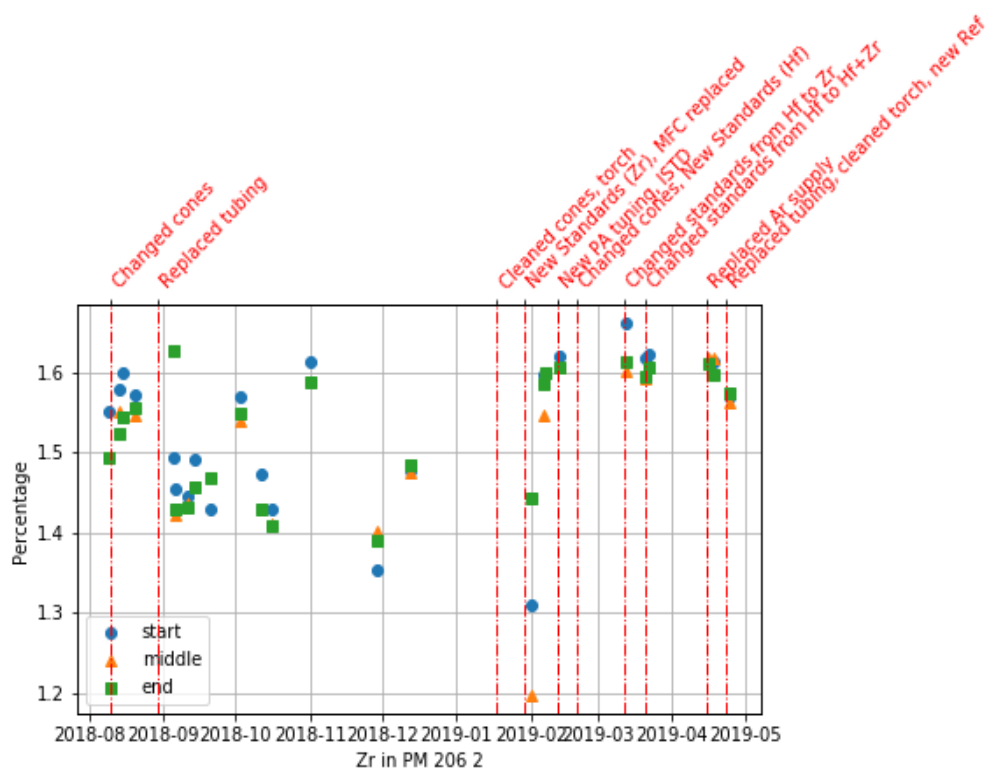


Figure 5.38 Time-scatter plot of Zr cation concentration variations over time of PM 206-2 sample at start, middle and end of the run.

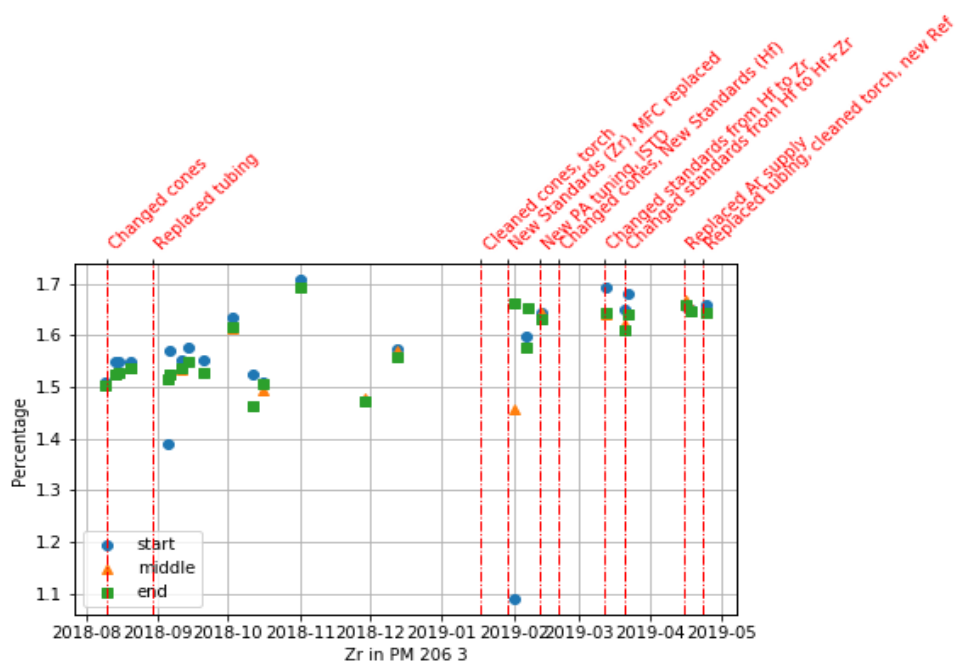


Figure 5.39 Time-scatter plot of Zr cation concentration variations over time of PM 206-3 sample at start, middle and end of the run.

Chapter 6

6.1. Conclusions

An in-depth study of different inline characterization techniques to monitor and control the production of REBCO tape has been conducted in this thesis. It also includes improvements in offline techniques like ICP – MS which plays an important role in determining the chemical composition of the thin films.

Inline XRD with a simple 1D detector was initially tested as a proof of concept for tracking the lattice parameter of REBCO film in an effort to deduce the density and orientation of BZO nanorods in heavily-doped REBCO tapes. Following a successful demonstration (albeit with limitations with regards to accuracy and resolution in the ability to discern tapes with closely matched lattice parameters), an upgrade was installed to the system to convert it into a 2D GADDS XRD architecture. This is a much more sophisticated system in terms of tracking not only nanorod density and orientation by tracking the BZO (101) peak directly, but also closely monitoring the primary REBCO (005) peaks and REO (400) peaks and providing a microstructural map of the entire tape along its length. The system has also proven successful in its ability to track degradation of primary and secondary phases due to localized hotspot regions which has been verified with HRXRD. Thickness variations due to non-homogeneous deposition conditions can also be readily tracked in terms of dropping count intensity. Apart from being able to track vital physical parameters, downstream performance of the tape in magnetic field has also been predicted with the streaking angle of the BZO (101) peak measured with the inline system. This is a vital performance metric and the ability to characterize the magnetic field performance of these tapes inline will play an instrumental role in fabricating tapes of long lengths with homogeneous properties. Chemical compositional correlations with the BZO (101) streaking angle has also proven to be successful and will play a pivotal role in determining the chemistry of the tapes inline which will again be of utmost importance in fabrication of long tapes with uniform properties.

Chemical compositional monitoring of vapor stream from an actual MOCVD evaporator has also been successfully demonstrated with a custom inline gas cell and FTIR system. A direct correlation of increasing signal strength of the IR fingerprint spectrum of every individual precursor molecule has also been demonstrated with increasing flow rates of the precursor molecules through the system.

The ICP-MS system has also been improved substantially in terms of accuracy, repeatability and reproducibility of experiments enabling the superconductor fabrication group at the University of Houston to obtain important correlations with magnetic field performance and stoichiometry of precursor preparation for the AMOCVD process. The installation of an Octopole Reaction system used primarily in Helium mode with Kinetic Energy Discrimination has proven successful in reducing the dispersion of measured data from reference samples. Calibration errors, which have long plagued the ICP measurements, have also been addressed through the use of novel quadratic curve fittings. Through the adoption of Continuous Calibration Verification and Statistical Quality Control techniques, a standardized system of measurement protocol is now in place to successfully track and conduct accurate experiments in the future.

6.2. Future Work

Based on the findings reported in this thesis, the following list of investigations is recommended for future scientific work:

1) Improvement in 2D algorithm peak detection – Variance in the data generated due to the noise in the current algorithm used in the inline 2D GADDS XRD system makes it hard to discern small variations in the properties of the manufactured tape. Improving this algorithm and reducing the noise when deducing the streaking angle of the BZO (101) peak can improve the robustness and accuracy of the system with shorter dwell times which translates to faster sampling rates and the ability to track finer changes across shorter length of manufactured tape.

2) Feedback control system using the FTIR – A proof of concept has been demonstrated in this thesis using a custom gas cell with an inline FTIR system. The ability to generate increased signal strengths with increasing flow rates demonstrates a clear cut path for a feedback loop of fine precursor compositional control using electronic injectors for individual precursor component. If this system can be realized and installed inline, this would be a huge leap forward in terms of improving the ability to control the output of the evaporator with a complex cocktail precursor.

3) Investigation into understanding the behavior of the zirconium standards - The biggest obstacle and blind spot in the ICP measurements is the behavior of the zirconium standards used for calibration curves. The variation in its signal strength with dilution is not clearly understood at the present. Investigating this behavior further with individual precursor standards as opposed to the conventional cocktail can shed some light on the type of behavior every individual molecule exhibits. Purchasing standards from different vendors and investigating their properties is definitely one approach to solve this problem. Investigations also need to be carried out to study the behavior of the ICP instrument with different dilution ranges of solvent used for the measurements.

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