Scanning Raman Spectroscopy for Reel-to-Reel Characterization of Second-Generation High Temperature Superconductors

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> Master of Sciences in Engineering Technology

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ABSTRACT

We have implemented fast Raman spectroscopy as a characterization method to predict, evaluate and characterize a variety of features of interest for Second Generation High-Temperature Superconductors (2G-HTS), including defect and composition characterization, as well as correlation with critical current density (J_c) over a wide extent of magnetic fields (0-14T) and temperatures (4.2-77K). A major factor for the successful implementation of this technique is the optimization of the scanning parameters that includes a large number of variables to reach the best spatial and spectral resolution needed to obtain detailed sample information. We first demonstrate the capability of implementation of scanning Raman to scan pristine and defective areas about 80 mm^2 on short samples utilizing a motorized XY motion stage. These scanning Raman results have been complemented with linear scans by two-dimensional x-ray diffraction (2D-XRD) in order to validate and cross-compare the results and the sensitivity of the technique. Next, the effectiveness of polarized Raman for evaluating the biaxial texture has been investigated in this work. Additionally, Raman features have been correlated not only to superconducting properties of the tapes acquired by vibrating-sample magnetization (VSM) but also with composition non-stoichiometry and nanorod dopant level of REBCO (rear earth = Gd, Y) thin films obtained by wavelength-dispersive x-ray spectroscopy (WDS) and induced coupled plasma (ICP) methods. Finally, the findings from these studies have been used to design a reel-to-reel system for in-line quality control of long-length coated conductors.

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CHAPTER 1. INTRODUCTION

Superconductivity is a phenomenon exhibited by certain materials of transitioning to near-zero electrical resistance when a temperature below the critical temperature (T_c) is reached, leading to the superconducting state. In these materials, electron transport possesses negligible energy losses by dissipation when subjected to an electric current lower than the critical current density (J_c). Such materials are known as superconductors, and they have a characteristic T_c that depends on the type of materials as well as their composition [1, 2]. According to their critical temperature, superconductors have been categorized as low-temperature superconductors (LTS) and high-temperature superconductors (HTS). In addition to the near-zero electrical resistance, superconductors are also characterized for their expulsion of magnetic flux when operating at a magnetic field lower than the critical magnetic field (H_c) specific for each material. [3, 4] Superconductors have widespread applications in many practical areas including medical (Magnetic Resonance Imaging) the energy sector including power cables, motors, generators, superconducting magnetic energy storage (SMES), etc. [4-6]

1.1. Brief overview of superconductivity

In 1911, superconductivity was first discovered by the physicist Heike Kamerlingh Onnes while working with liquefied helium. Onnes found that Mercury (Hg) behaves with zero electrical resistance under liquefied helium temperature (4.2 K), becoming the first element discovered to exhibit superconducting properties. [7] In the following years, more pure elements were found to show this behavior at temperatures below their respective T_c . Since then, the pioneering work of Onnes became well known among the scientific community and aroused a vast interest. In 1929, niobium exhibited the highest T_c of 9.25 K at the time. But it was not until 1941, almost 30 years later, that the first superconducting compound NbN was discovered with a T_c of 16.1 K. [8] The breakthrough in increase of T_c came in 1986, when the physicists Bednorz and Müller discovered the first system with the following stoichiometry: $La_{2-x}Ba_xCuO_4$. This system was categorized into the copper family (cuprate) superconductors, which differed fundamentally from superconductors discovered until then, including the Nb_3Ge alloy having a T_c of 23 K that was considered the highest at the time. This new material reported by Bednorz and Müller achieved a T_c higher than 30 K, becoming the first high-temperature superconductor (HTS). [9] [10] [11]

In 1987, shortly after LBCO was found, the scientist C.W. Chu discovered $YBa_2Cu_3O_{7-x}$ system at the University of Houston. This material is the first high-temperature superconductor holding a critical temperature of 93 K, significantly higher than the liquid nitrogen temperature (77K). This finding opened the door to a wide range of applications and potential industrialization, mainly because liquid nitrogen coolant is widely available and cost-effective compared to liquid helium. [1, 12] One year later, $Bi_2Sr_2CaCu_2O_8$ [13] and $Tl_2Ba_2Ca_2Cu_3O$ [14] compounds were discovered holding critical temperatures of 105 K and 120 K, respectively. Under standard pressure conditions, the highest critical temperature is held by $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8.33}$ at 135 K, while among the pressurized systems, $HgBa_2Ca_2Cu_3O_{8.33}$ can operate at 164 K under 30 Gpa of pressure. [15]

In recent times, other than cuprates, other superconducting material systems have been discovered. For example, MgB_2 can operate at $T_c = 39.2 K$ and H_2S has a T_c of 203 K under

90 Gpa of pressure as reported in 2001 and 2015, respectively [16][17]. Most recently, Ironbased materials systems have demonstrated superconductivity as well at T_c in the 8-56 K range. A brief summary of the evolution of superconductors discovered with a different critical temperature (T_c) over the years is presented in Figure 1 [8], where LTS stands for lowtemperature superconductor and HTS for high-temperature superconductors.



Figure 1. Superconductors and critical temperature (Tc) evolution since their discovery.

1.1.1. Types of superconductors

Superconducting state varies from one material to another, and it depends on crystal structure, stoichiometry, and the overall environmental conditions for each material. [6] Therefore,

superconductors can be classified according to their critical temperature (T_c) or their critical magnetic field (H_c) .

According to the critical temperature, superconductors are distinguished as low-temperature superconductors (LTS) at $T_c < 30$ K. On the other hand, the high-temperature superconductors materials (HTS) are characterized by their $T_c > 30$ K, most notably the systems with T_c above the liquid nitrogen temperature (77 K) as seen in Figure 1.

Superconductors are also classified according to their critical magnetic field (H_c). This classification refers to the maximum applied external magnetic field under which they still exhibit their superconducting properties. Based on their in-field behavior, they can be categorized as Type-I or Type-II, as described below.

Type-I superconductors exhibit only one critical magnetic field (H_c) upon which they transition from normal to superconducting state (typically occurring between 5 and 200 mT). Their superconducting mechanisms are explained by the Bardeen–Cooper–Schrieffer (BCS) theory [18]. Unfortunately, they are considered low-temperature superconductors as they are found in materials with T_c in the range of 0-7.1 K. Up to now, there have been identified only 27 pure elements with Type I superconductor behavior, where Lead (Pb) is the element with the highest operational $T_c = 7.2$ K [4].

Type-II superconductors are found in metal compounds, alloys, some complex oxide ceramics, and a few elements such as Vanadium (V), Niobium (Nb), and Technetium (Tc). These types of superconductors have two critical magnetic fields (H_{c1} and H_{c2}), the lower critical field H_{c1} and the upper critical magnetic field H_{c2} . Figure 2 summarizes the three field and temperature-dependent states of Type-II superconductors. Below H_{c1} , the Type-II superconductor is

superconducting, and the magnetic field is expelled entirely from the interior of the structure, essentially behaving as a Type-I. However, when exposed to higher magnetic field, the material shifts from superconducting state to a mixed state. At the mixed state, the material still behaves as a superconductor. But partial penetration of the applied magnetic field is observed until reaching the upper limit of the critical field H_{c2} which turns the material to the normal state.



Figure 2. H-T phase diagram for Type I and Type II superconductors.

The mixed state between H_{c1} and H_{c2} is characterized by the coexistence of normal and superconducting regions, where the formation of flux vortices surrounded by circular super currents allow magnetic flux to penetrate the superconductor. These vortices arrange in an ordered hexagonal lattice repealing each other. [19] However, when a current (J) is applied to superconductor under the mixed state, the vortices experience a Lorentz force ($F_L = J * \mu_0 H$) leading to vortex motion in a direction perpendicular to the applied current and magnetic field. If there is no barrier to avoid the movement of this vortices, dissipation of energy through the superconductor is observed. This results in the loss of superconducting properties. As the mixed state allows superconductors to stand stronger external magnetic fields, it becomes crucial to impede the motion of the vortices.[1] [19]. This problem can be solved by introducing structural defects created naturally or artificially during film deposition [3, 20]. Artificial defects, known as artificial pinning centers (APC), have a non-superconducting nature, and can be made out of additives or secondary phase precipitates such as Ba_2ZrO_3 (BZO), $BaHfO_3$ (BHO), $BaSnO_3$ (BSO) etc. [21] [22]

1.1.2. First Generation (1G) and Second Generation (2G) HTS

Shortly after the discovery of high-temperature superconductors, their use has become feasible for a wide range of applications in different fields. Those superconductors have applications ranging from research, to medicine, energy and military applications, among others. The first generation of commercially available high temperature superconductors (1G-HTS) were bismuth-based systems BSCCO-2212 and BSCCO-2223. Those systems were successfully produced in the form of wires and tapes. The BSCCO superconductors are fabricated from their respective oxide powder in a tube (OPiT) process adding relatively large quantities of silver around the superconducting tubes for stabilization purposes. Today we can see BSCCO tapes with lengths of up to 1 km. [23, 24]. However, due to their low irreversible magnetic field and high anisotropy, these wires are limited to low applied magnetic fields and operating temperatures below 25 K in order to maintain their superconducting properties. [25, 26] Additionally, the demanding amount of silver for their fabrication impose another disadvantage for the industrialization. [27]

The second-generation high temperature superconductors (2G-HTS) also known as coated conductors (CCs) were developed as a solution for the low performance in high magnetic fields

and to reduce the manufacturing cost presented by 1G-HTS. Contrary to 1G-HTS where multifilamentary wires were preferred, 2G-HTS consists of stacking layers growth in metallic substrates which lead the development and fabrication of flexible thin films. Among the 2G-HTS available systems, REBCO (rare earth (RE) = Y, Sm, Gd, Nd, Eu) have been the materials of choice for mass production due to its excellence performance, working temperature and relative affordability. Nowadays, it is possible to produce REBCO tapes in hundreds of meters long with successful applications for a variety of products.

1.1.3. REBCO Coated Conductors (CCs)

 $REBa_2Cu_3O_{7-x}$, rare-earth barium cooper oxide (RE = Y) was the first type II superconductor that is also a self-doped cuprate system. The $REBa_2Cu_3O_{7-x}$ was discovered by changing Lanthanum (La) from the LBCO compound for Yttrium (Y). This modification was responsible for the increase in critical temperature from 30 K to 90 K. Figure 3 shows the YBCO perovskite structure composed by two parallel CuO_2 layers per unit cell, which are believed to be the responsible for the superconducting characteristics [2]. This structure can have an orthorhombic or tetragonal form depending on oxygen content. The tetragonal framework is a non-conducting phase starving in oxygen x = 1, and orthogonal the structure has a complete stoichiometry x \approx 0 and it is identified as the superconducting phase. The differences in the CuO_2 frameworks are attributed to variations in the Cu and O atomic content (stoichiometry) [28]. In addition to the superconducting layer, three spacer layers corresponding to two BaO and one RE planes respectively are presented in this structure [3, 25].



Figure 3. Crystal structures of YBa₂Cu₃O_{6+x} (YBCO).

1.1.4. REBCO Deposition Methods

The fabrication of REBCO coated conductors involves the growth of textured metallic substrates by either Ion-Beam Assisted Deposition (IBAD), Rolling-Assisted Biaxial Texture Substrates (RABiTS), or Inclined Substrate Deposition (ISD), followed by the deposition of buffer layers. The buffer layers serve as a template to match the epitaxy for the superconducting layers. To achieve a high-quality crystal structure, the superconducting thin film is expected to grow epitaxially in the c-axis in the absence of ab-orientations and a minimum amount of grain boundaries. Finally, a protective silver layer is deposited on top to coating/seal the tape preventing potential damage from localized high heat and to protect against environmental conditions (see Figure 4). REBCO is the superconductor of choice over other cuprates due to its relatively high J_c and working temperature (77K) along with its simplified manufacturing. [20]



Figure 4. Typical REBCO tape structure consisted of Hastelloy substrate, $Al_2O_3/IBAD - MgO/Homo - Epi - MgO/LaMnO_3$ buffer layers, REBCO, and silver coating layer.

There exist multiple methods to fabricate high temperature superconductors (HTS), among which Pulsed Laser Deposition (PLD) and Metal Organic Chemical Vapor Deposition (MOCVD) are the leading techniques. The main reason is their potential to reproducibility and repeatability in terms of quality. Metal Organic Deposition (MOD) is also a common technique, but it has deficiencies such as to produce quality microstructure along the entire tape [29, 30].

Pulsed Laser Deposition (PLD) is a well-developed physical method that can be applied for different materials with high control stoichiometric. PLD has high reproducibility for complex structures. This technique consists of a pulsed laser oriented onto the target material's surface from which the material is evaporated and then sputtered on the superconductor tape/substrate where the superconductor film then grows. PLD is a line-of-sight process performed in vacuum. It is a relatively complex and expensive method and well known for its technical difficulties during deposition. This technique is rather recommended for limited areas and has been initially associated with throughput limitations. [31] [32] However, the technique has continued to evolve and increase in throughput continuously.

Metal-organic chemical vapor deposition (MOCVD) is among the leading techniques having high throughput for HTS. This method uses metal-organic chemical precursors containing the target elements (Y, Gd, Ba and Cu in the case of REBCO). The metalorganic vapors are carried by gases such as Argon and Nitrogen, and the precursors decompose on the heated substrate, leading to the deposition of the metal elements and removal of the decomposed organics in the gas phase. This technique offers high speed deposition rates and homogeneity, and it is ideal for epitaxial growth along the c-axis orientation. Unfortunately, the negative aspects of this method are their toxicity and elevated cost, in addition to the requirement of constant monitoring of pressure and temperature variables to achieve high quality deposition. [33] [34]

Metal-organic deposition (MOD) is a simple process that does not require vacuum. The deposition is carried out by dip-coating, spraying, or spinning the substrate into the chemical solution. Once the optimum thickness is reached, the material is annealed to precipitate the right microstructure(s). MOD is a non-toxic method that can be implemented under atmospheric conditions. This technique has versatility in terms of the choice of materials and the uniformity of the structure. However, it is limited to a few precursors and critical thickness that may promote cracking during heat treatments and handling. [35] [36]

1.1.5. Artificial pinning centers (APCs) in REBCO coated conductors

As previously mentioned, the superconducting properties of HTS can be enhanced by the growth of natural defects such as voids, point defects, dislocations, precipitates, etc. Alternatively, by introducing artificial pinning centers, in-field critical current can be significantly enhanced. [25, 37] REBCO crystals are primarily anisotropic with limited

coherency having along the c-axis a strong pinning center structure. This improves the critical current density when compared to pristine REBCO crystals. [38] Therefore, the artificial pinning centers into the REBCO matrix are today the defect of choice and they are engineered within the superconductor by different methods. In addition, the deposition methods have tremendous versatility for doping using rare earth elements or secondary phases. [25] On the last two decades, the scientific community have focused on the identification of the perfect configuration in terms of shape, density, dimensions, among other parameters to optimize the pinning centers with the sole intention to maximize J_c . [20, 21, 37, 39]

In recent studies, introduction of secondary phases such as $BaZrO_3$, $BaTiO_3$, Al_2O_3 , RE-211, etc. have demonstrated to enhance the critical current density (J_c). However, to approach an optimal efficiency of the APCs control of growing conditions, deposition temperature, and doping additions is crucial during the process. [40] [37] Here is where this work resides, particularly in the determination of the Raman features capable of identifying the ideal superconductor.

1.1.6. Characterization Methods for REBCO films

The industrialization of 2G-HTS long tapes needs the use of proper characterization and quality control methods. It is paramount to guarantee the quality of the tape in a cost effective and competitive manufacturability level. Currently, there are different methods implemented to evaluate the quality and properties of the thin film structure. However, the extent of the analysis is often reduced to selected areas. Additionally, some of these techniques are destructive or time consuming such as in the case of inductively coupled plasma mass spectroscopy (ICP-MS), x-

ray diffraction (XRD) or wavelength dispersive spectroscopy (WDS) that can take hours to be performed and the information provided corresponds to micro-metric areas. Therefore, high throughput and non-destructive quality control methods are required for the complete understanding of the material's repeatability, reproducibility, and overall integrity to yield consistent performance. This is the key factor to guarantee high quality of the superconductors at a competitive price.

Raman spectroscopy is a remarkable technique for materials characterization. Firstly, subtle information regarding crystallinity, chemical bond vibration, polymorphism, foreign phases among other more intricated characteristics within the crystals can be determined. Secondly, this technique does not require special, labor-intensive, time-consuming sample preparation. Next, the acquisition time can be as low as on the order of seconds, what makes this technique potentially much faster in comparison to 2D-XRD, WDS or TEM. Finally, when confocal Raman microscope is utilized, spatial resolution at the sub-micron level can be achieved. As a result, specific areas containing embedded features or grains bellow the detection limit of conventional techniques such as XRD or Neutron Diffraction (ND) can be characterized. [41-43]

1.2. Motivation

The need for scaling up worldwide production of 2G-HTS at affordable cost to meet the potential demand has been a major challenge. More precisely, manufacturing of REBCO long tapes demands high yield with uniform structure along the tape. The complexity of the deposition method requires a precise control over the process parameters to avoid negative

effects on the homogeneity and performance of the conductor making the fabrication of 2G-HTS an intensive, complex, and expensive labor. Particularly, the I_c current for the entire tape is not determined by the highest I_c within the tape, but rather by the lowest. Additionally, defects in the tape can allow the propagation of mechanical deficiencies such as delamination, cracking, coil quench, etc.[34, 44, 45] avoiding these defects is mandatory to develop commercial superconductors. Therefore, emphasis on quality control is a priority to successfully produce long superconductors to maximize and guarantee competitive I_c performance at large scale that will lead to true industrialization. In this thesis, we have proposed Raman spectroscopy as a versatile characterization method and potential inline feedback tool for process control. The results demonstrate the potential of the technique to be implemented as both off-line and in-line characterization and process control method for 2G-HTS coated conductors.

1.3. Thesis outline

This thesis is divided into five chapters. Chapter 1 presents a review of superconductivity and evolution of superconductors in general, provides a detailed review of REBCO superconductors and elaborates on key aspects of characterization. Finally, a detailed discussion on the motivation for this study is provided.

Chapter 2 presents a literature review focusing on Raman spectroscopy, its principles, and its relevance and potential importance for characterization of REBCO superconductors. In addition, the key Raman spectroscopy parameters and data analysis tools including tool standardization are discussed in detail.

Chapter 3 elaborates on the experimental methods implemented in this thesis and on the optimization of the relevant Raman spectroscopy parameters for the samples investigated in this study. The experimental setup for Raman scanning is discussed in this chapter, as well as the details of other supporting characterization techniques used in this study.

Chapter 4 focuses on the results obtained with Raman spectroscopy, WDS, ICP, XRD, as well as on the correlation studies between the results obtained by the listed techniques, with emphasis on correlating the Raman spectroscopy results to superconducting performance $(J_c(B,T))$ and material composition (WDS, ICP). In addition, two dimensional Raman maps of selected defective regions are presented and analyzed in detail, in order to evaluate the level of detail obtainable with the technique. The chapter is concluded by presenting the details of a customized reel-to-reel scanning system that has been developed and designed in the course of this study and which will be fabricated and implemented immediately upon conclusion of this study as the next step in the continuation of this study.

Chapter 5 gives a summary of the work and the findings of the feasibility study of implementing Raman spectroscopy as both inline of offline method for characterization and quality control of 2G-HTS, followed by suggestions for future work.

CHAPTER 2. LITERATURE REVIEW

Over the last few decades Raman spectroscopy has been widely used in different fields, from life sciences to thin films, carbon, semiconductors, energy, medicine to mention a few. Due to its simplicity, adaptability, and high throughput, this technique facilitates the identification of material structure, grain orientation/texture, secondary phases, foreign elements, induced stresses, defects, and surface damage, among others. Above all, this technique offers quantitative as well as qualitative information of the investigated material [2] [46] [47]. Raman spectroscopy is based on Raman effect discovered by Chandrasekhara Venkata Raman and his research partner in 1928 and was awarded the Nobel Prize in 1930. This effect is the interaction of monochromatic light with vibrating molecules within the sample. When the molecule is excited by a photon (i.e., laser) it produces a scattered light with same or different frequency as the incident light known as elastic or inelastic scattering, respectively. The inelastic scattering or Raman scattered component is a small fraction of the scattered light with an occurrence about 1 in 10^7 of the emitted photons and has a different wavelength than the incident beam. The change in frequency is what provides information characteristic of each molecule. In addition to the scattered light, fluorescence can be also observed when strong light is used, and it has a detrimental effect over Raman signal. [48]

2.1. Raman Scattering Principle

When a photon interacts with the molecule, a distortion of the electron cloud is generated for a short period; this is called the 'virtual state'. Since the virtual state is not stable, the photons will

immediately scatter to a more stable state. However, the interaction with the atom will have different responses. In the event, this interaction does not generate any atomic vibration and the energy level of the scattered light is the same to the incident light. The process is known as elastic Rayleigh scattering. On the other hand, if molecular vibration is generated and a change in energy level is produced it is called inelastic Raman scattering and this is an inelastic effect. [49] There are two different responses of the Raman inelastic scattering: in the first one, the scattered light losses energy (excited to a higher energy level) and its frequency increases. The phenomenon is recognized as Stokes Raman scattering. On the second case, if the molecule gains energy (excited to a lower energy level) and its frequency decreases, it is called Antistokes scattering. Figure 5 shows the three different processes a molecule undergoes when excited from its energy ground level by the incident light. In common practice, one usually observes Stokes Raman scattering rather than anti-Stokes Raman scattering because it is a stronger scattering. Equation (1) is used to calculate the difference between the scattered and incident light known as Raman shift and is given in units of cm^{-1} , this equation relates the energy level spacing of the vibrational mode. [46] Raman spectrum is presented as Raman peaks Intensity (photon) vs. Wavelength (Raman shift cm^{-1}), and those peaks represents the energy characteristic of a vibrational mode.

Raman Shift =
$$\left(\frac{1}{\lambda_{incident}} - \frac{1}{\lambda_{scattered}}\right) \times 10^7 \ cm^{-1}$$
 (1)

Where $\lambda_{incident}$ is the wavelength of the incident light (nm) and $\lambda_{scattered}$ is the scattered light (nm)



Figure 5. Energy-level Diagram of the Rayleigh and Raman scattering.

Sample information through Raman spectroscopy can be interpreted as follow: the number of photon counts (e.g., peak intensity) may offer information about concentration of particles within the sample under very specific circumstances, but overall gives information of presence of the molecules investigated. In some cases, when the material is doped, the intensity can be used as a measure of the respective disorder in the lattice. The peak position is the characteristic Raman frequency of the material. Additionally, shift of the peak to lower or higher frequencies can be related to stress/strain induced in the material, effects of temperature, pressure, or distortion within the structure. When deformation of the crystal structural occurs, there is loss of the crystal symmetry inducing forbidden peaks due to the breakdown of the selection rules, which become visible on the Raman spectrum. Finally, Full Width at Half Maximum (FWHM)
analysis offers information regarding structural disorder such as defects, foreign element substitution, and sample crystallinity (see Figure 6). [50]



Figure 6. Diagram of a Raman band and the respective information that can be used for material's characterization.

Raman scattering in crystalline materials is produced and perceived when the following selection rules are satisfied by the scattered light: (i) polarization rule: the molecular vibration generated after the passing of the incident light must change the polarizability of the molecule. In other words, if the molecule change is polarizability a change in shape, size and orientation is observed, then the molecule is said to be Raman active, and the difference between the frequency of the scattered light and the incident light (v' - v) must be ± 1 wavelength to be considered a vibration transition of first order. On the other hand, a difference $\Delta v = \pm 2, \pm 3$ are overtones with a weakly spectral band allowed by the selection rule.[51] (ii) Energy conservation rule $E_i - E_f = h(v' - v)$, where (v) is the frequency of the incident light and

(v') is the frequency of scattered light, and Ei and E_f are the energy of the initial and final state of the molecule, respectively, and (h) Planck's constant: The difference between the incident light and scattered light need to match the difference of the energy state $(E_i - E_f)$; as a consequence any frequency of light can be utilized.[52]

As Raman scattering is originated by the vibration of the central part of the molecule or nucleus, it becomes important to understand the vibrational states that can be observed. This vibration occurs only along the chemical bond connecting the nuclei, and can be symmetric, asymmetric, or bending vibration, which are considered as the normal modes. There are other more complex modes such as rocking, scissoring, twisting vibrations.[51] Symmetry vibration takes place when the atomic motion is back and forward along the bond, which is also known as in-phase stretching motion. In the event that one atom bond shrinks while the other stretches, this mode is understood as the out-phase stretching or asymmetric vibration. Finally, bending vibration is experienced when the motion of the atoms occurs in the direction perpendicular to the bond. Figure 7 shows examples of the vibrational modes for a CO_2 molecule. The analysis of molecular vibration becomes a major challenge for complex structures. As a result, the description of complex structures is typically limited only to their most characteristic features.

[46]



Figure 7. Normal vibrational modes of a CO_2 molecule.

A few additional remarks should be considered when using Raman spectroscopy. First, Raman signal is stronger when the vibration of the molecule is symmetrical, meaning the material is an ideal crystal. However, when defects or damage is presented on the structure, loss of periodicity, disorder of the lattice, and reduction of the symmetry may result in violation of the selection rules and reduction of photon lifetime. As a result, forbidden Raman bands become visible, and broadening of the Raman-active bands will be also induced. Second, Raman shift is closely related to strain/stress, as well as structural disorder. Hence, when the crystal lattice is strained, or structurally altered, Raman bands shift to lower or higher frequencies as well as alter in intensity as the defect becomes more pronounced. [50, 53]

2.1.1. Raman Polarization and Raman Tensor

The polarizability of the molecule (α) is determined by interaction between incident light and distortion in the electron cloud. After such interaction, the emitted light is polarized along a

plane or one direction, described as dipole change in the molecule in Cartesian coordinates. Equation (2) expresses the dipole change induced by the polarizability of molecules.

$$\mu = \alpha E \tag{2}$$

The dipole moment (μ) and the electric field (E) hold the three components of the Cartesian planes x, y and, z. Then equation (3) must be written as:

$$\begin{bmatrix} \mu_x \\ \mu_y \\ \mu_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yx} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$
(3)

where α_{ij} matrix is called the polarizability tensor. A molecule vibration is Raman-active if after interaction of the incident light with electron cloud generates a change in any of the components of the polarizability tensor.

Polarized Raman offer useful insight not only for molecular structure but also to determine orientation of ordered structures. In the cases relevant to most HTS, the Raman tensor for orthorhombic and tetragonal phases are presented in Table 1. Vibrational modes allowed by the symmetry of the Raman tensor would be seen in specific scattering configuration of the incident and scattered light. The common notation used to define the scattering configuration is known as Porto notation. An example of this notation is $x(y,z)\bar{x}$ backscattering configuration, where x and \bar{x} denotes the directions of the propagation of the incident and scattered light, and y, z the direction of the polarization of the incident and scattered light.

Orthorhombic уу zz yx уz B_{1g} B_{2g} A_{g} B_{3a} Tetragonal $\begin{pmatrix}
xx \\
xx \\
zz
\end{pmatrix}$ xу xy -xx-xy(xy B_{2g} A_{1g} $A_{2,g}$ B_{1q} xz` хz zxzx E_g E_{g}

Table 1. Raman tensor for orthorhombic (D_{2h}) and tetragonal (D_{4h}) groups taken from [54, 55]

In order to test the level of texture or epitaxy in the superconducting tape, one can use polarized Raman. A clear example is the presence of in-plane and out-of-plane texture on REBCO crystals that can be determined by using polarized Raman. [56]

2.2. Characterization of REBCO Superconductors

Raman spectroscopy has been implemented practically since the discovery of high temperature superconductors due to its versatility and suitability for in-situ analysis. It is evident that a clear advantage of Raman is its potential for non-destructive analysis and the fact that samples can

be analyzed without the need of sample preparation. Raman can operate under external conditions such as low or high temperature. For example, it has been recommended for low temperature conditions where the phonon can freeze and the structure analyzed purely based on structural and bonding characteristics [57], under presence of magnetic or electric fields, and high pressure without affecting the results. [54] In other words, Raman is the spectroscopy of choice not only for in-line manufacturing, but also as a preventive quality control or even a process control tool (feedback provider) in an industrial setup.

At this point the focus is to investigate the family of rare-earth cuprates that are high temperature superconductors such as REBCO (RE= rear-earth, Y, Gd, Nd, Sm, Eu, Tb). These superconductors are subject to recent resurgence in interest for many practical applications due to superior superconducting properties in high magnetic fields much above those obtainable by LTS, as well as potential operation in a wide range of temperatures from 4.2 K up to liquid nitrogen level (77 K). [12] Many Raman studies of REBCO systems have been conducted to analyze the effect of oxygen content, thin film texture, substitutional elements, impurity effects, among others.

The typical spectra of REBCO include five Raman-active modes in addition to the forbidden modes that are allowed when the selection rules are broken due to defects, impurities, or lattice disorder. The expected Raman active modes for orthorhombic and tetragonal structure are presented in Table 2.

Mode	OrthorhombicTetragonalFrequency (cm^{-1})Frequency (cm^{-1})		Assigned to	
(<i>Ba</i>)	116 cm ⁻¹	118 cm ⁻¹	Barium motion	
(<i>Cu</i> ₂)	149 cm ⁻¹	142 cm ⁻¹	Vibration of copper	
$(0_{2+}/0_{3-})$	335 cm ⁻¹	340 cm ⁻¹	Out-of-phase Oxygen atoms (O_2) and (O_3)	
$(0_{2+}/0_{3+})$	433 cm^{-1}	450 cm^{-1}	In-phase Oxygen atoms (O_2) and (O_3)	
(O_4)	500 cm^{-1}	475 cm^{-1}	Apical Oxygen Atom	

Table 2. Raman modes assigned for a YBCO structure.

Forbidden bands when the structure of the crystal is distorted are commonly seen at 230 cm^{-1} , 600 cm^{-1} for oxygen disorder, and cation disorder by foreign element substitution respectively [58], or in case of presence of impurities, the peaks at 300 cm^{-1} , 380 cm^{-1} , 630 cm^{-1} for *CuO*, Re_2O_3 , AND *BaCuO*, respectively have been identified. [59] In this section, a review of Raman scattering studies conducted to analyze the effects of oxygen content, thin films texture, cation disorder, secondary phases, induced stress/strain, on high-Tc superconductors is presented in detail. In

Figure 8 a schematic representation of the five Raman peaks observed for REBCO structure is shown.



Figure 8. Graphical representation of the Raman active modes along c-axis and their respective vibration.

2.2.1. Oxygen Content and Texture Quality

Oxygen content and texture/orientation are two important factors characteristic of REBCO system, and features related to that are observed in a typical Raman spectrum. These features are key to understand the overall crystallographic structure orientation and ultimately its superconducting state. In other words, in a production line, we can relate this feature to a rough estimate of the general state of the superconductor. $YBa_2Cu_3O_{7-x}$ when (x = 0) possess an orthorhombic structure where the oxygen chains are fully completed, and this structure has

superconducting properties. Conversely, when this oxygen chain is empty, the structure changes to non-superconducting tetragonal phase (x = 1). According to the selection rules, there are 15 modes allowed for YBCO-O, and 10 modes for REBCO-T structures [54, 60]. However, only the modes parallel to the c-axis are analyzed in common practice, which are the five Raman-active bands mentioned above.

- YBCO-O (orthorhombic) = 15(5A_g + 5B_{2g} + 5B_{3g}), corresponding to the motion of Ba, Cu₂, O₄, O₂₊/O₃₋ (out of phase), O₂₊/O₃₊ (in phase) along the c-axis (A_g), a-axis (B_{2g}), and b-axis (B_{3g}).
- YBCO-T (tetragonal) = $10(4A_{1g} + B_{1g} + 5E_g)$, c-axis (A_{1g}, B_{1g}) and a/b -axis (E_g) .

In another study, Iliev et al [43] show the coexistence of a microdomain in addition to the Ortho-I, Ortho-II, T reported in YBCO thin film. Such structure named tetragonal average T'. Such structure was observed when the sample was underdoped (oxygen deficiency) and exposed to high temperatures during local laser annealing. The respective Raman bands are found at 139, 234, and 590 cm^{-1} . Those bands are more evident when the material is exposed to temperatures between 548 and 663K. The intensity of the peak between 231-265 cm⁻¹ increased as the oxygen content decreases. This behavior is explained as the breaking of the (O_2) chains during annealing process. The authors indicate advantages of Raman spectroscopy over conventional techniques such as XRD and neutron diffraction (ND) including detection of multiphase structure with oxygen content dependency, and particle size (resolution) below

(~100 lattices). Therefore, Raman is significantly more accurate and has a broader application together with higher simplicity than XRD and ND.

Chen et al [61] studied ultra-thin $YBa_2Cu_3O_{7-x}$ films, thicknesses starting from 16, 28, 40, 80, to 200 nm, using micro-Raman spectroscopy. The results show an increase in the intensity of the (O_4) mode as the thickness decreases. This variation was attributed to change of the film texture instead of oxygen content, mainly because all samples were well oxygenated under same conditions. Moreover, the experimental observations showed a correlation of a-axis grain oriented when the intensity of this mode increases, and a reduction of the O_{2+}/O_{3-} mode intensity is observed. This effect is related to the c-axis grains orientation. A novelty in this work is the presence of the following bands: 307, 464, 560, and 630 cm^{-1} that are attributed to defects and impurities. In particular, the 307 cm^{-1} band is associated to the BZO layer. The 464 cm^{-1} and 630 cm^{-1} bands are characteristic of CuO, and $BaCuO_2$ impurities, respectively. Noteworthy, these bands are extinguished as the thickness of the superconductor reaches 200nm. In conclusion, the defects and impurities are presumably found at the surface and the interphase with the substrate.

Camerlingo et al [62] analyzed YBCO film exposed to heat treatment between 20-300°C. Raman measurements revealed the expected peaks for well oxygenated samples at room temperature at 336 cm⁻¹ (O_{2+}/O_{3-}) and 500 cm^{-1} (O_4). However, the superconducting phase exhibited degradation as temperature reach 200°C that is identified by the shifting of the (O_4) mode to lower frequencies between (488-497 cm^{-1}). This shift is presumably the result of a reduction in the oxygen content, which is also a promoter of the transition to a tetragonal structure. Another band presenting similar effects is the one identified at 420 cm^{-1} (O_{2+}/O_{3+}) in highly stoichiometric samples. This band shifts to ranges near $450cm^{-1}$ in oxygen deficiency structures.

Kim et al [63] implement Raman spectroscopy for characterization of Gadolinium Barium Copper Oxide (GdBCO) thin films deposited by Pulse Laser Ablation (PLA). These films were analyzed after being subjected to growing temperatures between 790 and 810°C and oxygen partial pressure ranging from 100 to 700 mTorr. Raman characterization demonstrated that the samples with the highest critical current density showed their active bands between 326-329 cm^{-1} , 444-447 cm^{-1} , 500-503 cm^{-1} when oxygenated at 300 and 500 mTorr and exposed to 810°C, respectively. In addition, this group observed peaks at 234 cm⁻¹ and 605 cm⁻¹ that were assigned to oxygen stretching vibrations and *BaCuO* secondary phases.

2.2.2. Disorder in the REBCO lattice by Foreign Phases and Impurities

The current search for materials capable of carrying substantial current with higher critical temperatures (T_c) is well known. This has opened the opportunity to use a wide variety of elements for doping, and the curiosity to explore secondary phases or intermediate transformations during the fabrication process to improve the superconducting properties. All those differences (e.g., doping, impurities) can be explored with Raman, which can conclusively help in the understanding of the role on the structure and performance.

Kakihana et al. [64] studied the effect of doping the Y123 compound with different amounts of Cobalt (Co) $YBa_2Cu_{3-y}Co_yO_{6+d}$ ranging from $0 \le y \le 0.5$. Raman measurements show the presence of $BaCuO_2$ impurity that is untraceable by X-ray diffraction. Another two characteristic bands observed with Raman are found at 275 and 550 cm^{-1} and they are more visible as cobalt content increases. Those bands are attributed to the distortion of the CuO chain by the presence of Co addition that causes characteristic vibrations of copper and oxygen, respectively.

Maroni et al. [65] investigate the correlation between cation disorder and the drop out of critical current density (J_c) in 1.5-1.7 µm thick YBCO films deposited by PLD and MOD techniques. Raman characterization on samples growth by PLD method show that the cation disorder band at $590cm^{-1}$ changes with film thickness. This behavior was observed in a range between 0.4 and 0.6 μm . However, after 0.6 μm , the cation disorder peak kept constant, and (J_c) measurements followed the same trend as the cation disorder did. On the other hand, YBCO films deposited by MOD showed no cation disorder in samples with thicknesses below 0.9 μm . However, for thicknesses > 0.9 μ m, secondary phases were identified at 600 cm⁻¹ (Ba_2Cu_3O) and $630 \text{cm}^{-1}(BaCuO_2)$. An important result from this study is that no obvious correlation between increasing cation disorder and critical current density (J_c) dropout was observed in the MOD samples. In a subsequent study, Maroni et al. [66] compared 0.9 µm thick REBCO films doped with Zr in the range from 2.5 to 10 % mol. Zr. Raman results along the tape showed small variation of the cation disorder peak (600 cm^{-1}) for Zr additions up to 7.5% mol. However, addition of $Zr \ge 7.5$ % mol. resulted in sharp strengthening of cation disorder while promotion of Ba-Cu-O was seen to increase progressively from bottom to top. Neither cation disorder nor Ba-Cu-O showed a clear correlation to the critical current density (J_c) measurement taken for different Zr amounts.

Aytug et al. [67] also analyzed the effects on dopped YBCO with different amounts of zirconium deposited by MOCVD method. This group showed that when zirconium additions change up to 7.5% mol a strong band at 300 cm^{-1} appears, which has been assigned to CuO impurity, together with increase in the cation disorder peak intensity. They observed a strong correlation between the dropout on the critical current density (J_c) and development of CuO secondary phase.

YBCO growth by TFA-MOD technique at 750, 775 and 800°C were characterized by Raman spectroscopy.[68] The results showed dependency of secondary phases development as the growing temperature increases. These secondary phases were assigned to CuO ($300cm^{-1}$), $Ba_2Cu_3O_{5.9}$ ($600 cm^{-1}$), and $BaCuO_2$ ($630 cm^{-1}$). Interestingly, these phases were not observed by using XRD, either due to weak intensity or more likely due to textured orientation. In the latter case, the peaks would be observable by 2D-XRD. In either case, the detection of these phases by Raman provides insight into the sensitivity of the method to characterize superconductors. In this study no clear correlation between critical temperature (T_c) or critical current density (J_c) and secondary phases was observed. This group was not able to confirm if the secondary phases can act as pinning centers due to the absence on the trend between secondary phases and superconducting properties. They attributed this result to possible degradation of the morphology at the surface of sample as the temperature increases.

2.2.3. Stress-Strain

Residual stresses on YBCO thin film deposited by pulsed laser deposition technique are affected by film thickness particularly in the range between 80 and 2000 nm. [69] The main

changes are found on the band at 440 cm^{-1} characteristic of the O_{2+}/O_{3+} (in-phase), which is almost absent for thinner samples. The Raman band intensity enhances as the film reaches 2000nm. The surface temperature and deposition affect the formation of c-axis grains, well oriented c-grains are an indication of the high quality YBCO films. According to the result obtained by Raman spectroscopy, the authors determined that when the peak at 335 cm^{-1} , assigned to c-grains, is no longer visible and the mode at $500 cm^{-1}$, corresponding to a-grains, sharpens, it is the evidence or consequence of formation of a-grain oriented film texture. In reference [69], a methodology to measure the quality of REBCO film texture is presented. In this method, the ratio between the intensities of (O_{2+}/O_{3-}) and (O_4) is studied. The results suggest that when I_{0203} / I_{04} > 1, the c-axis formation is dominant. Alternatively, if I_{0203} / I_{04} < 1, the a-grain texture dominates. The stress analysis can be determined based on the shifting of (O_{2+}/O_{3-}) peak. In thinner samples (80 to 320 nm) tensile stress component is seen when the band shifts to lower frequencies usually from 337 cm^{-1} to 335.6 cm^{-1} . Consequently, as the sample reaches 1 μ m and the stresses are apparently released the band shift near 335 cm^{-1} , a value associated to the orthorhombic structure. Apparently at thicknesses of 2 µm, the band shifts back to 336.8 cm^{-1} indicating a new back-transition that is again in tension. A drastic (J_c) drop is observed in samples of 2 µm or thicker, which is attributed to a-axis grains formation along with the tensile stress caused in the structure.

2.2.4. **REBCO Manufacturing measurements**

The successful implementation of in-line reel-to-reel Raman spectroscopy for $YBa_2Cu_3O_{7-x}$ has been reported in [70]. The group analyzed tapes of 1.25m length and thicknesses between

300 nm and 1000nm. These samples were measured during a continuous heat treatment from 650°C (start temperature) to 740 °C (transition temperature). In the early stage of the process after reaching the transition temperature, presence of secondary phases such *CuO*, *BaCeO*₃ at 300 cm^{-1} and 350 cm^{-1} , respectively, were observed. These bands strongly decrease in intensity when reaching 34 min into the chamber, giving place to development of characteristic bands at 145, 330, 450 cm^{-1} for the tetragonal structure. In the range from 60 to 80 min of exposition at 740°C pure tetragonal structure impurities free is dominant, and the authors defined this range as the 'sweet spot' or the optimal growth conditions. However, for exposition times greater than 80 min new impurities Ba-Cu-O related were observed suggesting degradation of the YBCO structure. With this study, the authors demonstrated there is a strong correlation between the maximum critical current density (*J*_c) and the structure of the samples from the optimal conditions found. Thanks to these important findings, the authors suggest Raman spectroscopy is a great tool for structure characterization that could replace transport measurements at cryogenic temperatures.

The on-line testing of YBCO films produced by MOCVD was first reported by Maroni et al. [71] In this work is presented a successful system where Raman spectroscopy is capable of analyzing 10 m/h of tape. The scanning mode implemented here was set to collect single spectra from the center of the tape. The results exhibit the characteristic peaks for a YBCO thin film besides the existence of secondary phases such as $BaCuO_2$ at 610 cm^{-1} , and CuO at 300 cm^{-1} . The texture quality of the tape was provided from the ratio Io₄/Io_{2O3}, where values >1 indicates possible c-tilted grains or presence of a-axis grains that may result in loss of superconducting properties. It is also reported a successful correlation between Raman bands and tapes' performance. The critical current drops in a 7:1 ratio when the intensity between CuO is three times the intensity of (O_{2+}/O_{3-}) mode.

Miller et al. [72] used Raman spectroscopy to analyze REBCO thin films deposited by MOCVD in a six-track system. For a multiple pass fabrication method, pronounced bands of tilted grains, secondary phases, and cation disorder were observed after the second pass. It suggests that fabrication of multilayer tapes increases the probability of development of a-axis oriented grains affecting superconducting properties.

Aytug et al. [22] study YBCO thin film deposited by MOCVD technique when temperature and oxygen flow were varied. The characterization analysis was carried out in a reel-to-reel system. Raman results showed that when the temperature changed from 920 to 960°C and oxygen flow was about 1.11 min⁻¹, there is small trace of secondary phase as well as oxygen and cation disorder observed on the structure. However, when the oxygen flow increases to 2.1 min⁻¹ at lower temperature 920°C, a change in the O_4 mode intensity is observed indicating presence of a-grains. The strength of the cation disorder and CuO impurity bands were also recorded, which was attributed to the structure distortion due to the increase of oxygen content. This finding was correlated with the drop of critical current density.

2.3. Experimental Aspects in Raman Spectroscopy

Micro-Raman spectroscopy has been demonstrated to be a powerful technique for a broad range of applications in both science and industrial fields. The continued advancements in Raman technology have resulted in reaching the submicron resolution. Further advances include the confocal Raman spectroscopy as well as 2D and 3D mapping.

In contrary to the improvements, one of the most common mistakes in this technique is lack of the equipment optimization, standardization, and the right configuration to properly acquire data. This results in unsatisfactory performance and poor quality in the final output. In order to produce a system with the needed reliability for industrial use in delicate environments such as superconductor tapes, the parameters and limitations must be well established. One should consider the optimum compromise between spatial resolution and scanning speed of paramount importance, as well as optimizing the spectral resolution. [73] In addition, many other aspects such as minimum feature size, the compromise between the degree of selectivity by confocality and sensitivity to defocus and others must be carefully considered in order to obtain meaningful scans. Finally, data extraction and analysis is of equal if not critical importance. For example, correlating the Raman features to superconductor performance at various temperatures and fields of interest, superconductor composition, sensitivity of Raman spectra to parameter variations during film deposition and related features are of utmost importance if Raman is to be utilized successfully as either offline or inline characterization and/or process control tool.

2.3.1. Spatial Resolution

For Raman spectroscopy, spatial resolution is a key factor to determine the analyzed area. Therefore, defining the right spot size is crucial when secondary phases inside the sample or other special features need to be precisely discriminated. This parameter is a function of the following factors: objective magnification, numerical aperture, laser wavelength, and sampling steps.

The laser spot is estimated by the crossover (waist) diameter in the XY focal plane given by equation (4), where NA is the numerical aperture of the objective lens, and λ is the wavelength of the incident light. The numerical aperture is a key element of the microscope objective lens, this parameter describes the capabilities of the objective to focus and collect light. For higher resolution shorter wavelength and larger NA should be utilized.

$$D = \frac{1.22\lambda}{NA} \tag{4}$$

The selection of the laser excitation wavelength, and numerical aperture will depend on sample's thermal absorption coefficient and surface topography. The sample absorption parameter will define the ability of such material to absorb light. If this parameter is high, the material is more prompt to absorb photons leading to thermal degradation. For example, when short wavelengths are used in dark samples, it is more likely to burn the sample as well as promote higher fluorescence.[74] Regarding the sample topography, it is important to consider the subtle changes of sample surface in order to avoid dramatic variation on defocus that may result in poor signal acquisition. These issues can be prevented or solved by selecting longer wavelengths or lower laser power density. In the case of samples with changes on topography, objective lens with lower numerical aperture may be helpful. In today's market a broad range of laser wavelength can be found from 244 nm to 1064 nm.[50]

2.3.2. Spectral Resolution

Spectral resolution is the other factor to consider in Raman spectroscopy as this defines the accuracy of the spectrum. The spectral resolution depends on focal length, grating and laser wavelength. In this case it is assume that the spectrometer is properly focused. Thus, resolution can be improved by selecting a grating with higher groove lines; however, the signal intensity decreases. To compensate herein one need to increase acquisition times. For example, a 600gr/mm grating can scan larger ranges than a 1800gr/mm at the expense of the resolution. Spectral resolution is also affected by the wavelength as the resolution depends on the spatial size of the features to be resolved as well as the excitation energy. In other words, longer wavelength is associated with lower resolution. The CCD camera plays a role for the spectral resolution as the smaller the pixels the higher the resolution. Finally, the focal length, which is the distance between the focusing mirror and the detector, should be considered if higher resolution is required. For this reason, some systems are known as true confocal that has a focal length or an optical fiber/mirrors configuration of at least 760 mm in length. Alternatively confocal systems take advantage of apertures that eliminate the beam dispersion and improve resolution. Yet, the true confocal tends to be a better a system. [50]

2.4. Data Acquisition and Data Analysis

Data processing is an essential aspect to correctly interpret Raman results. In this section, the main factors that must be considered for accurate interpretation of the spectral features is presented.

2.4.1. Signal to Noise Ratio (S/N)

The signal-to-noise ratio (S/N) is the most important factor when dealing with spectral features due to the accuracy of peak fitting will strongly depend on this parameter. Low (S/N) or noisy data compared to high (S/N) data can never reach the same accuracy. Therefore, to proceed with spectral processing, the crucial requirement is to work with data with minimized noise as excessive noise might result in misleading outcomes. The principal source of noise considering a background free measurement are shot noise (the signal by itself), thermal noise (electrons thermally created for temperature $> -60^{\circ}C$), and readout noise (noise from the signal amplifier and the digitalization process). [74] Therefore, in order to achieve an acceptable S/N, the shot noise should dominate the spectrum, and the other two noises must be kept as low as possible. The best way to reduce the thermal noise is by keeping the CCD temperature below $-60^{\circ}C$ and shorter acquisition times. The readout noise can be control by using high quality readout amplifier with sufficient speed that allows to reduce the acquisition times. In other words, it becomes essential to optimize system parameters such temperature, acquisition times, laser power etc. In principle, there is no lower limit to noise reduction, as there is no lower limit in acquisition time - the shorter the acquisition time the faster and/or more spatially resolved scans can result. Ideally, infinitely fast scans would be preferred. As such, noise levels approaching zero are desireable. More practically, signal should dominate by orders of magnitude over noise even for shortest acquisition times. The most practical way to achieve this is to increase incident laser power to the maximum possible level without burning the sample. Sample burnout can be reduced by reducing power density which translates to increase in sampled spot size. This in turn results in decreased spatial resolution. Depending on the minimum feature size that needs

to be resolved, this compromise between laser power, power density, spot size, minimum feature size, scan speed and spectrum S/N quality can be optimized.

2.4.2. Cosmic Rays Removal

Cosmic rays (spikes) are high energy protons generated from outer space that move through the space at nearly speed of light and interact with the atoms in the earth atmosphere. In Raman spectroscopy this unpredictable and random event are read out by the detector (e.g., CCD) and displayed as narrow features (spikes) of high intensity on the recorded spectrum. Analysis of these peaks must be done carefully to avoid confusion with real peaks characteristic of the sample evaluated. Usually, those peaks can be discriminated by them with (single digit cm⁻¹) or by collecting data numerous times in the same spot. Currently, spectrometers are equipped with software that provides cosmic rays removal when collecting data or when processing the results. A simple way recommended to prevent the acquisition of cosmic rays is by having two or more accumulations per spot. It is also recommended to reduce exposition times to the minimum but maintaining a good signal-to-noise ratio. [75] Alternatively, the spectra averaging method is well accepted as a removal method (see Figure 9).

2.4.3. Background Removal

The most important aspect in the Raman spectra is the signal to noise ratio, particularly in terms of mapping that is the primary objective of this work. The Raman spectrum is collected along with other signals that are the result of several responses and can contribute negatively to loss in spectral details. This includes signal broadening or weaker signal-to-noise ratio. Higher

background can be detrimental for quantitative and qualitative analysis of the result. For this reason, it is important to improve the signal quality by implementing background correction. This eliminates the spectral deviation resulting from unwanted interferences. The sources of the background signal can be attributed to the CCD detector sensitivity or true signal background, including fluorescence among other effects (see Figure 9).

Background from the CCD detector is generated for the dark currents that involves parasitic residual quasi-static electros in the detector. The elimination of this type of background is relatively simple as it is constant and should be subtracted as a constant value in the detector. True signal background on the other hand is directly associated with the material characteristics or the substrate. To remove this background it is necessary to use mathematical algorithms as indicated in reference. [75]



Figure 9. Background and cosmic rays' effects on Raman spectrum. Taken from [76]

2.4.4. Peak Fitting

Peak fitting is carried out to extract in a more precise and accurate way the acquired spectra to avoid misinterpretation. The benefit of peak fitting is in measuring the peak width, peak

position, and peak intensity among other spectral features from a spectral data. There are different peak functions that can be used for spectrum fitting, and it would depend on the nature of the sample (solid, liquid or gas), and the analyzed molecules as well. The Raman line shape can have features of Gaussian and Lorentzian profiles, or Voight character, which is a convolution of Gaussian-Lorentzian curves. Therefore, for spectral peak fitting different methods can be used as shown in Table 3 [75] [77] For greater detail in the functional form of Gaussian, Lorentzian, and Voigtian profiles refer to [78]

Filter	Information content (results)		
Linear Fit	- Slope - Offset		
Quadratic Fit	 Peak Position Curvature Peak Intensity Peak Position 		
Gaussian fit Lorentzian fit	 Width Integrated Intensity Offset 		
Pseudo Voigt fit	 Peak position Width (Gaussian and Lorentzian Integrated intensity Offset Profile Shape 		

Table 3. Fitti	ing filter	for spectra	l data.	Taken from	[75]
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2.5. Statistical Analysis

Statistical analysis is implemented to understand the relationship between a set of collected data with the purpose of uncover possible trends or patterns. Scientists and engineers have used statistical methods to determine whether one variable has influence over another and make an approximation of the experimental behavior of uncertain data. Applying statistical methods leads to more accurate experimental design and reliable conclusions from the acquired data. In this thesis, statistical correlation will be utilized to study possible correlation between Raman features and superconducting performance.

2.5.1. Pearson's Correlation

Pearson's correlation is one of the most common methods used to evaluate the strength of the relationship between two variables. The correlation among the variables is associated by a unitless coefficient that fall between -1 and 1. The degree at which the data cluster around the regression curve (usually a straight line) determines the correlation among quantities and it is known as the correlation coefficient and is commonly expressed with the Greek character rho " ρ ".

Figure 10 shows different examples of the data with variation of the correlation coefficient value, where a perfect positive correlation is equal to one and has a positive slope which indicates the two values moves in the same direction. On the contrary, a perfect negative value of the correlation coefficient is equal to -1 with a negative slope, which means as greater one value is as lesser the other going in opposite directions. A correlation coefficient equal to zero (0) implies not relation between the paired data. [79] Now, it is important to understand that a regression is a mathematical algorithm that relates the sum of the square of the distances between the collected data and the regression curve. In other words, two points equidistance to the regression curve have the same effect, but negative to each other having a complementary null contribution to the regression.



Figure 10. Scattered plots of different cases of correlation coefficient. Taken from [79]

The correlation coefficient is represented by the letter ρ and can be found by the equation (5), where \bar{x} , and σ_x and \bar{y} and σ_y are the mean and standard deviation of x and y variables, respectively. x_i and y_i are the correlated variables, N is the scalar observations.

$$\rho(x,y) = \frac{1}{N-1} \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\sigma x * \sigma y}$$
(5)

There are some factors that must be taken into consideration when using the correlation coefficient.

- 1. Each pair of values are normally distributed, which ensure linearity, this can be seem in a scattered plot between X and Y. Otherwise, results can be misleading.
- 2. Results must not have missing values
- 3. Interchanging the values of x and y, multiplying by a positive constant, or adding a constant to each value has no effect on the correlation coefficient.
- 4. It is highly important to consider the physical meaning of outliers presented on the scattered plot because they can mislead the interpretation of the results. In the case, the origin of these outliers cannot be explained as a consequence of experimental error and

then removed or corrected. It is highly recommended not to use the correlation coefficient to analysis the data. [80]

2.5.2. Hypothesis Test

As mentioned above, the correlation coefficient is a value to measure the strength of the linear relationship between a data paired. However, to determine the significance of the correlation coefficient, it becomes necessary to conduct a hypothesis test. The hypothesis tests allow one to decide whether the significance of the correlation coefficient is significantly strong to use the linear model to fit the population. The degree of certainty obtained by hypothesis testing is given by a number called the p-value, which falls between 0 to 1, and this value is interpret as close to zero or significantly different from zero. Nevertheless, to evaluate the significance of the correlation coefficient, the p-value must be compared to a significance level number (α) that is commonly set at 0.05 or 0.01 but ideally should be between 0.02 and 0.03. This number indicates the probability of concluding correlation between two variables when it can be possible no real correlation exist. Therefore, in the event p-value is ≤ 0.05 the correlation is statistically significant then it can be concluded the correlation is different from zero and the linear relationship between the two variables must be real, but if p-value > 0.05 the correlation is not statistically significant then it cannot be concluded the correlation is different from zero. To perform a hypothesis test there are five steps that must be followed:

1. Specify the null hypothesis (H_0) , which indicates the changes observed on the samples are due only to random variation. Therefore, there is no correlation between the variables. In this thesis for REBCO thin film analyzed, the null hypothesis is set as there

is no correlation between Raman measurements and critical current density (J_c) , or any other two pairs of variables, if the correlation coefficient (ρ) is equal to zero.

$$H_0: \rho = 0$$

Define the alternate hypothesis (H₁), which suggests the changes observed on the samples must be related to the experiment and represent the entire population. Consequently, predicts relationship among the variables. Following the example if (ρ) is different from zero then correlation between the two variable is likely truth.

$$H_1: \rho \neq 0$$

- Perform an appropriate statistical test where the p-value would be reflected. Equation 5 would be used for this study.
- 4. Set the significance level α to evaluate the statistical significancy, here we suggested between an $\alpha = 0.05$.
- 5. Evaluate the p-value at the significance level set, $p \le 0.05$ to reject the null hypothesis and consider likely possible the alternative hypothesis.
- 6. Draw conclusions whether or not the initial hypothesis is supported. Therefore, if we found that (ρ) is equal to zero there is no correlation between Raman measurements and critical current density (J_c) values obtained in this thesis. On the other hand, if (ρ) is different than zero then a certain degree of correlation can be determined.

CHAPTER 3. EXPERIMENTAL AND METHODOLOGY

In this chapter, the experimental techniques implemented for characterization of REBCO tapes are presented. Special attention is given to Raman spectroscopy, as the primary objective of this thesis is to find a powerful, non-destructive, and rapid method for characterization and quality control during manufacturing of long length REBCO tapes. Additionally, Raman measurements are complemented with two-dimensional x-ray diffraction (2D-XRD), wavelength dispersion spectroscopy (WDS), vibrating sample magnetization (VSM), and inductively couple plasma (ICP) analysis. VSM and ICP measurements were not carried out as part of this study but were instead measured separately in the past. Those results are stored as part of the database of the 2G-HTS samples produced at University of Houston and were used to study correlation between the measurements done in this study including Raman spectra, 2D-XRD and WDS and the previously collected VSM and ICP results. The VSM and ICP results presented here were conducted as an independent research and by other members of the team. This data is used in the current work for comparison purposes and to strength the correlations among results.

3.1. REBCO Samples

REBCO thin films between $0.5 - 8 \ \mu m$ thick were used in this research. These samples were deposited on Hastelloy/Al₂O₃/IBAD-MgO/Homo-Epi-MgO/LaMnO3 substrates using the Advance Metal Organic Chemical Vapor Deposition (A-MOCVD) system with direct ohmic tape heating supplied by AC or DC current and lateral cross-flow of the precursor gas. [81] All of the samples were synthesized by the Advanced Manufacturing Institute located at the

University of Houston¹. The films composition consists of standard precursor solution with molar ratio of Gd:0.65, Y:0.65, Ba from 1.9 up to 2.35, Cu:2.6. Besides that, 0, 5, 15 mol.% range of Zr and 0, 5, 20, 25 mol.% range of Hf were added as doping elements for growth of BZO nanorods and Re_2O_3 precipitates.

A total of 48 samples were investigated in this work. The films dimensions were approximately 3.3 x 3.5mm with thicknesses ranging from 0.5 to 8 μ m, typically and most frequently on the order of 4 μ m. The samples were characterized using WDS, Raman and 2D-XRD. The Raman maps were obtained from an area of about 1mm². The WDS presented is the average of 9 measurement per samples using a beam diameter of 10 μ m. Samples used for defects analysis were >4 μ m thick, and dimensions about 12 x 10 mm, where defects were introduced by disturbances created during fabrication process. The samples used for this analysis are shown in Figure 11. These flaws were recognized in first place by Scanning Hall Probe Microscopy (SHPM) at 77k, 0T measurements and then the regions with losses in magnetic properties were cut and subjected to scanning by Raman spectroscopy. Finally, polarized Raman was implemented for evaluation of the biaxial texture in two samples that were previously investigated by XRD ϕ – scans and the in-plane orientation showed significant variation. This experiment was carried out mainly to prove the feasibility of Raman for the study of the in-plane texture. Shown in Figure 11 are the samples used in the present work.

¹ https://ami.uh.edu/



Figure 11. Example of the analysis conducted to collect the database (a) Raman characterization area of 1 mm^2 scanned, and 225 spectra collected. (b) WDS analysis, 9 points of 10µm diameter per film were taken. (c) Sample scanned for defective areas 11 x 7.5mm. (d) Samples for texture analysis where a single spectrum was captured but rotation of the samples was changed from 0° to 45°.

3.2. Raman Spectroscopy

The purpose of using Raman spectroscopy in this thesis is to evaluate its promising capabilities as a characterization and quality control method for off-line and in-line applications during fabrication of REBCO tapes in an industrial set up. Scanning mode is implemented for microstructural analysis of wider areas as well as for detection of defected regions. Besides that, polarized Raman single spectra have been collected for biaxial texture analysis. Two different Raman set up have been implemented in this study. One using unpolarized Raman light, when both incident and scattered light are not polarized in an specific direction [82], and second using polarized and depolarized light, where polarized refers to incident light and scattered light are parallel planes, and for depolarized, both lights are perpendicular to each other.

3.2.1. Unpolarized Raman Spectroscopy Measurements

Microstructural characterization and defects analysis were performed in Raman scanning mode utilizing an X-Y motion control stage. These measurements were taken at room temperature using a confocal micro-Raman spectrometer (XploRA, Horiba Jobin Yvon) with no polarizers, which means light comes in all direction. The Raman spectrometer is equipped with a set of three excitation lasers 532 nm (green), 638 nm (red), 735nm (infra-red). In addition, three diffraction gratings are available 600gr/mm, 1200 gr/mm, and 1800 gr/mm. The spectrometer is coupled to a BX41 Olympus microscope with 10x, 50x, and 100x objective lens, and uses air-cooled CCD detector. The nominal laser power of this equipment 5mW can be modified by incorporated attenuation filters, enabling a range from 100%, 50%, 25%, 10%, to 1%, being 100% full power, i.e., the filter number or percent refers to transmittance rather than attenuation. Figure 12 shows the Raman system used for this study. In Table 4 the final parameters for Raman measurements after turning up the system with a sufficiently high signal-to-noise ratio and avoiding surface damage is presented

Parameters	Database Samples	Defected Samples	
Scanned Area	1x1 mm ²	7.5x11 mm ²	
Steps	70x 70 µm	100x 100 µm	
Laser (nm)	638	638	
Objective (Mag)/NA	50x/0.75	50x/0.75	
Grating (gr/mm)	1200	1200	
Filter (%)	25	25	
Power (mW)	1.25	1.25	
Hole	500	500	
Slit	100	100	
Accumulation	1	1	
Scans	225	8436	
Acquisition Time Per Scan (s)	2	2	
Total Time (s)	504	19000	

Table 4. Raman spectrometer parameters selected for samples characterization.

*Incident laser beam perpendicular to the surface and laser spot $< 2\mu m$

The spectra were processed utilizing a custom developed code for detection of aberrant spectra, optimized background subtraction, optional averaging of neighboring spectra, and peak fitting to the Voigt function.



Figure 12. Raman spectrometer system

3.2.2. Polarized Raman Spectroscopy

As explained above, the main feature of using polarized Raman is that crystal orientation can be found as well as crystal texture by changing the polarization of light. Therefore, polarized Raman was implemented to demonstrate the feasibility of this method to obtain information of the in-plane and out of plane texture. Two samples grown using the A-MOCVD system with different in-plane texture have been evaluated in order to determine the c-fraction and inplane texture using a state-of-the-art triple Raman spectrometer T64000 (Horiba Jobin Yvon) equipped with a liquid nitrogen cooled CCD. Raman measurements were conducted at room temperature using a 488nm Ar⁺laser with 3mW laser power, and a 100x objective lens. Raman scattering was recorded in polarized $z(xx)\overline{z}$ and depolarized $z(xy)\overline{z}$ backscattering geometry following Porton Notation. [82] For in-plane measurements, the samples were positioned at 0° and 45° angle, rotating the sample with respect to the axis perpendicular to the film surface.

3.2.3. Wavelength Disperse Spectroscopy (WDS)

Wavelength Dispersive Spectroscopy (WDS) is used for compositional analysis based on the emission of characteristic x-rays from the material when interaction with an electron beam. In comparison to energy dispersive spectroscopy (EDS) that is also used for composition analysis, WDS has a detection limit <100 pmm which allows the analysis of trace elements present in the samples. Additionally, WDS has a higher spectral resolution than EDS, which means it is possible to resolve the presence of smaller amounts of specific elements when compared to EDS. In EDS the presence of those elements could be hidden in the background or under overlapped signals due to systematic resolution. A main disadvantage of WDS is the data acquisition time, sample preparation and overall, the technique is more labor-intensive. In addition, it is a vacuum technique and as such it is not readily adaptable to reel-to-reel continuous measurements, at least not for commercially available systems. In order to generate a precise correlation study we have selected WDS over EDS.[83] [47] Elemental analysis of the samples was accomplished by using a JEOL JXA 8600 microprobe, with a spot diameter of 10µm, beam current of 35nA and spectral resolution of 35 eV, time per point was \approx 9min, and nine point s per samples were acquired.

3.2.4. Inductively couple plasma (ICP)

Inductively couple plasma is implemented for measuring material elemental composition. It uses atomic emission for the determination of elements concentrations. ICP is a destructive method with good precision, however, few elements have poor sensitivity, which make difficult their detection in comparison with other techniques. [84] Film composition for this study were

analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP). However, all samples were not investigated by this technique. Therefore, WDS was used as the main compositional analysis method on this study.

3.2.5. Vibrating-Sample Magnetization (VSM)

Vibrating-sample magnetization (VSM) is used to measure the magnetic moments of a sample when subjected to vibration perpendicular or parallel to an externally applied magnetic field. VSM method has a higher throughput and accuracy than transport measurement, where larger sets can be measured. However, a typical deviation of 0° to 3° is obtained when using VSM due to fact that measurements of the in-field performance is performed at magnetic field perpendicular to the tape (B⊥tape) instead of measuring the magnetic field perpendicular to the c-axis direction (B⊥c). In addition, the J_c criterion is much lower than the criterion used for transport measurements. As a consequence, a direct comparison of the J_c values obtained from these two methods cannot be made. [85] Contact-free magnetic analysis was conducted using a vibrating sample magnetometer (VSM), Quantum Design DynaCool PPMS in the direction B⊥tape at 0-14T and 4.2-77 K at the sweep rate of 20mT/s. samples size were in average 3.2x3.5mm with side b > a, the current density J_c was calculated from the magnetization results using equation (6). [86]

$$J_c = \frac{20\Delta M}{a\left(1 - \frac{a}{3b}\right)} \tag{6}$$

Where a and b are the samples sized b > a, and ΔM is the hysteresis in the magnetization curve M(H) given by $\Delta M = (-M^+)$ being M^- the decreasing and M^+ the increasing magnetic field.

3.2.6. Two-dimensional X-Ray Diffraction (2D-XRD)

Two-dimensional x-ray diffraction (2D-XRD) is a novel technique. The main difference compared to conventional XRD is having detectors in two dimensions. This permits to interpret the analysis of 2D images and 2D diffraction pattern. It means the diffraction is not limited to the diffractometer plane as in the case of conventional XRD (or 0D-XRD); instead the whole range of the diffraction ring can be measured. [87] 2D-XRD is used for phase quantification, structure analysis, crystal orientation, residual stress analysis. In the case of REBCO characterization, 2D-XRD has proven to be a rapid and non-destructive method for rapid characterization of superconducting tapes and to assess their overall quality, crystallinity, and defects. This technique is particularly useful for BZO nanorods analysis. [37] In addition, using the GADDS system, the out of plane and in-plane texture can be estimated as well.

In this work, 2D-XRD was performed point wise to analyze defects of interest with step increment of 0.5 mm across a straight line along the tape width using a state-of-the-art system with microfocus Cu source, Monel optics and 0.5 mm collimator (Bruker). The in-plane texture of REBCO films were analyzed by XRD-φ-scan measurements.
CHAPTER 4. RESULTS AND DISCUSSION

In this chapter, the study performed will be presented in the following sections:

Section 4.1: a systematic study is implemented to identify the most precise operating parameters for the Raman system to lead a satisfactory mapping of REBCO tapes. Key considerations are laser wavelength, laser power, microscope optics, detector gratings, acquisition time, accumulations, among others.

Section 4.2: Feasibility for 2D-mapping on REBCO tapes using an X-Y moving stage. Also presented is the development of an automated code for data processing. The main goal with this code is to eliminate signal background, cosmic rays' effect and aberrant spectra with the purpose of achieving a more accurate peak fitting.

Section 4.3: The capability of Raman scanning is proved by mapping defected samples to precisely correlate performance to microstructural characteristics. In addition, 2D-XRD linear maps for the same samples will be performed and compared with the features observed by Raman maps.

Section 4.4: Polarized Raman for studying of biaxial texture, c-axis and a-axis grains orientation, is presented with the intention of analyzed REBCO tapes texture. Consequently, it is compared to 2D-XRD ϕ -scan measurements.

Section 4.5: a database with Raman measurements is developed for correlation of in-field superconductor performance. This study intent to analyze samples with different composition and magnetic properties and look for remarkable changes on Raman spectra.

Section 4.6: a design of a reel-to-reel system for future expansion of this work is presented.

4.1. Raman Spectroscopy Instrumentation

The versatility of Raman spectroscopy in comparison with other spectroscopy methods has allowed its application in a broad range of fields such as for analysis of solid, liquid, and gaseous samples with a minimum or no sample preparation. This technique is used for quantitative analysis by measuring the frequency of the scattered radiation (Raman shift) or qualitative analysis by measuring the intensity of the scattered light. Nonetheless, implementation of this technique requires control of several parameters to obtain high quality data regarding the unique information of material. For this section, the Raman equipment parameters are evaluated to provide the most adequate set up for sample analysis. Consequently, the variables consider here and their effects over REBCO tapes are system power source 5mW, lasers 532nm and 638nm, objective magnification lens X10, X50, X100, gratings 600gr/mm, 1200gr/mm, 180gr/mm, power attenuation filters 1%, 10%, 25%, 50%, 100% (100% indicates full power), and confocal pinhole 100 and 500, among these variables other considerations will be evaluated such as the defocus effect and topography sensitivity.

4.1.1. Effect of Laser Wavelength, Excitation Power, and Numerical Aperture

When devices are equipped with different lasers, it becomes essential to select the correct laser wavelength and laser power excitation to obtain good signal to noise ratio and simultaneously avoid sample burning and fluorescence, which are detrimental effects to the sample and the Raman spectrum resolution and quality. Therefore, selection of the laser characteristics is fundamental in this work. It must be considered that Raman intensity is proportional to λ^{-4} of the excitation laser, where λ is the lasers wavelength. Then a shorter wavelength results in higher Raman intensity. On the other hand, the Raman signal is also proportional to excitation power, which means higher power leads to higher intensity of the spectrum and possible thermal degradation of the sample investigated. Therefore, the excitation power must be lower than the absorption and thermal conductivity coefficient of the samples to avoid overheating and detrimental effects. In the case the coefficient of absorption is unknown, the recommended practice is to begin working with lower excitation power in combination to acquisition times, as energy emitted is equal to the product of power and time, so that by controlling these two parameters sample damage is prevented.[74] In conclusion, the selection of laser wavelength and laser power depends on sample characteristic. In addition to this, the laser power density transfer to the sample also relies on the numerical aperture (NA) of the microscope objective, where higher numerical aperture can lead to higher power concentration in a smaller spot diameter increasing the chance of sample damage. For instance, when a fixed wavelength of 532nm and excitation power is used with two different objective magnifications say x100 and x10 with NA=0.95 and NA=0.25, the spot diameter achieved is about 1µm and 2.5µm, respectively, which means more power would be transmitted to the smaller spot size in this case 1µm. Also, it is important to highlight the numerical aperture also have an important effect on signal intensity. Therefore, lower numerical aperture results in poor signal intensity requiring longer acquisition times that for R2R applications these parameters should be evaluated carefully in order to achieve good signal intensity at minimum acquisition times and prevent sample degradation as well.



Figure 13. Impact of laser wavelength, laser power and numerical aperture on REBCO thin film. Analysis was done at same laser power excitation 5mW and acquisition time 10s (a) Laser 532nm and NA 0.25. (b) Laser 532 and NA 0.90. (c) Laser 638nm and NA 0.25 and (d) Laser 638nm and NA 0.9.

From Figure 13 it is clear that the full power of the laser used in this study (5 mW) is detrimental for the sample at 10s exposure interval (50 mJ) when using either 532 or 638nm laser wavelengths, which makes necessary to implement attenuation filter to decrease the emitted power. Additionally, it is proved that higher numerical aperture (NA) can concentrate more

power on the laser spot leading to more severe damage. However, it is seen in Figure 13(d) that for a larger laser wavelength of 638 nm in comparison with 532nm for the same laser power the damage is much lower. Also, using a lower numerical aperture such in Figure 13(c) no damage on the sample is detected. Therefore, from these results, where the amount of power needs to be controlled, the laser 638 nm has been selected as the candidate of choice for our research. Surely, 532 nm could potentially be used at much shorter exposure time to achieve similar S/N ratio at higher scan speeds. However, in order to make the results also comparable with most of the literature on Raman spectroscopy applied to REBCO, we have selected 638 nm for most of the work in this study. Nevertheless, the selection of the laser is more complex than focusing on laser wavelength, power, and numerical aperture (NA). It is also crucial to consider exposition time, defocus, and more critical the signal to noise ratio that at the end is what would allow one to interpret the data acquired.

By implementing different attenuation filters the laser power can be reduced and the sample degradation avoided. Shown in Figure 14 are the Raman spectra of REBCO samples after being exposed to laser 638nm during 5s, using a x100 microscope objective. Here the laser power was attenuated by filtering the laser light at 10%, 25%, 50% and compared to full power. The micrographs corresponding to each spectrum are displayed to show possible surface deterioration. The results show that in order to lower the chance of burning the sample for the 638nm laser, a 25% filter (1.25mW) must be utilized. The same test was carried out for laser 532nm and the required attenuation for no detrimental effect was seen using a 10% filter (0.5mW). However, it becomes necessary to evaluate the SNR obtained when these two lasers are employed under the conditions determine for each of them due to interpretation of the

Raman spectrum will depend on peaks definition. The main goal of this exercise is to optimize the relation between laser power attenuation and acquisition time to establish the right parameters for the ideal signal to noise ratio (SNR).



Figure 14. Raman spectra of REBCO sample after being exposed to laser 638nm, and x100 objective lens for 5 seconds and different attenuation filters. When 10% and 25% filter was used no sample, damage was observed.

Shown in Figure 15 is the signal to noise ratio evaluated for 638 and 532nm lasers for acquisition times ranging from 0.1s to 100s, and different filters. It is important to highlight that the results include burned samples. Therefore, 532 nm laser burned the samples even for a 10% filter (0.5mW) for acquisition times >10s. Unfortunately, for times < 10s the SNR was not sufficient to get the right quality of the spectrum. For this reason, the 532 nm was rejected for

the present study. In the case of the laser 638nm, for filters 50% (2.5mW) and 100% (5mW) the samples were degraded. Nevertheless, when 25% filter (1,25mW) was used, a satisfactory SNR for almost each acquisition time was observed. In conclusion, the selected parameters for power exposure, acquisition time, and laser wavelength that yields acceptable SNR of \approx 15dB are the laser 638 nm with an attenuation filter of 25% (1.25mW) of nominal power, 2 seconds of exposure, and x50 objective lens. Finally, the energy transferred to the REBCO film without sample damage is given by equation (7). [88], which for 1.25mW and 2s this translates in 2.5mJ of Energy to the samples.

$$E = P * t \tag{7}$$

Where P is the average power of the laser (W), and t is the exposition time in seconds.



Figure 15. Signal to noise ratio of representative spectra for different times, 100x objective lens and laser power attenuation levels for LEFT: 532 nm and RIGHT: 638 nm laser.

4.1.2. Effect of Diffraction Grating

A grating is a fundamental component of a Raman spectrometer, which has an important effect on the Raman spectrum resolution, as well as over the acquisition times. These diffraction gratings collect the scattered light that is reflected into the microscope and then each detected wavelength is dispersed in a slightly different angle onto the CCD detector. The number of grooves or lines per millimeter determines de resolution of the spectrum. Gratings with high number of lines per mm result in better resolution and more definition of the characteristic peaks. However, higher number of lines also means the signal is distributed over a broad number of CCD pixels, requiring longer collecting time. For example, in case a range from 100 to 1600 cm^{-1} is desired to be analyzed, a 600 gr/mm would spend one window to finish the acquisition, but an 1800 gr/mm would require three windows instead to collect the data for the same range, which means the acquisition time is triplicated. Not to mention that every window and shutter open/close process results in further dwelling times. Furthermore, as the lines are of finite width, progressively more signal is attenuated as the line density is increased. Thus, higher diffraction gratins also leads to lower Raman intensity. [46, 89] In this analysis the gratings 600gr/mm, 1200gr/mm, 1800gr/mm were tested. Shown in Figure 16 is an example of raw data obtained from the same sample for each grating used. It can be observed that as the grating line density increases, peaks become narrower (higher resolution), but a drop of signal intensity as well as the background is also noticeable. The reduction of background may be convenient for data analysis; however, reduction of Raman peak signal may lead to unsatisfactory results. In the case of 600gr/mm grating, broadening, and shifting of peaks is observed, which in an ideal system must not occur. Additionally, higher background is

observed. On the other hand, the 1800gr/mm required three acquisition windows to collect all data resulting in trifold increase of acquisition time compared to the lowest grating. This may be acceptable for single scans. However, for this study where maps of bigger areas are going to be collected, the need of lower acquisition times and acceptable peak resolution is crucial. Finally, based on the results reported, the optimum grating selected is 1200 gr/mm.



Figure 16. Comparison of spectra acquired from 600 to 1800 gr/mm grating. Peaks become narrower with finer grating, additionally background, and intensity drops. On the other hand, shifting and broadening of peaks occurred for lower grating.

4.1.3. Effect of Confocal Pinhole

Raman scattering is a very weak effect, and the number of scattered photons is limited to the emitted energy. Nonetheless, the development of confocal Raman spectroscopy has lead to

improvement of Raman acquisition efficiency. The term confocality is defined as having the same focus onto a sample, which means the object is measured from the same focal plane. Using confocal microscopy in combination with Raman spectroscopy have several advantages, such as higher spatial resolution, higher spectral resolution, higher depth of focus for transparent samples, and most important the use of confocal holes helps to block the out of focus light (background) allowing high quality of the acquired spectra. [90]

4.1.3.1. Fluorescence

It is well known that fluorescence background is a major issue in Raman spectroscopy. This effect can be six orders or more of magnitude higher than the Raman scattering light. Therefore, with no control over this effect, the fluorescence signal can overcome the Raman signal and the final spectrum becomes hidden under the fluorescent spectrum. To minimize this issue, confocal holes are beneficial as the collection of the signal is limited to the near vicinity of the confocal depth only. In non-confocal methods it is possible to detect fluorescence from above or below the confocal plane.[74] Thus, when a small hole is used, a higher resolution with better Raman spectrum features are achieved and the fluorescence background is minimized. Figure 17. compares the effect of using a 100 and 500 hole for acquisition of Raman signal. Higher peak definition and reduced background levels are achieved when the 100 hole is employed. On the other hand, a bigger hole size allows a higher laser throughput at the expense of increased fluorescence. Additionally, the bottom two spectra correspond to the 50% filter, in which a clear weakening on the Raman signal is observed due to 50% reduction in power, and there is still observable background for the 500 hole. In conclusion, the data observed in this

experiment shows that confocal Raman spectroscopy is an excellent technique when higher resolution and a background suppression is needed.



Figure 17. Comparison of collected spectra of a REBCO sample when filter attenuation of 50% and 100% of the nominal power is used, and the confocal hole size varies from 100 and 500, for an acquisition time of 5s and a grating1800 gr/mm.

4.1.3.2. Spatial and Spectral Resolution

The spatial resolution for a confocal Raman microscopy is crucial for detection of samples details at the sub-micron scale. The higher the spatial resolution the more information of the sample structure can be obtained. The numerical aperture of the microscope lens and the excitation wavelength are key factors to consider when high spatial resolution is needed. Theoretically, the spatial resolution S is defined by laser wavelength and NA aperture of the

objective magnification as shown in equation (8). However, this is given for standard light microscopy but in Raman spectroscopy some the interaction of the light with different interface may reduce this resolution. For example, a 638nm laser and x10 objective lens with NA = 0.90, gives a theoretical spatial resolution of about ≈ 442 nm. Therefore, selection of these parameters would mainly depend on the level of detail needed in the investigated sample and its respective structure.

$$S = 0.66 * \frac{\lambda}{NA} \tag{8}$$

In addition to spatial resolution, the laser spot diameter plays a role when studying heterogeneous samples. In particular, the laser spot contributes to determination of sampling step, relationship that will allow to determine the optimum balance between resolvable or detected feature size and scanning speed. From equation (9) the diameter of the laser spot in the focal plane can be determined.

$$d = 1.22 * \frac{\lambda}{NA} \tag{9}$$

Presented in Figure 18 is a scanning map of REBCO tape where an area of $10\mu m \times 7\mu m$ was analyzed using an objective lens x100, NA = 0.9 and 638nm laser wavelength, which gives and diameter spot and a spatial resolution ≈ 865 and 422 nm, respectively. It clearly shows the system capability to identify features at the sub-micron level. In this map two a-axis grains oriented in an embedded c-axis oriented grains matrix were identified. In general, highly detailed maps can be obtained from very small feature, however, a pair-sampling relationship, where the diameter laser spot is equal to the step size compromises acquisition time, resulting in longer times of data acquisition. Consequently, with the purpose of scanning long continuous length of REBCO conductors over 12 mm width this selection becomes unsuitable. Instead, an approach that provides average information with satisfactory scanning step and spatial resolution is employed. We have found good relationship between spatial resolution, scanning steps, and acquisition time under the following conditions: laser 638nm, an x50 lend NA = 0.75 and scanning step 100x100 μ m. However, it should be noted that ideally, the laser spot size should match the step size. Sampling an area with a spot much smaller than the area itself can render random 'binary' signal not representative of the area itself. For example, if the area in Figure 18 is sampled by only one spot, say 1x1 μ m, it could randomly hit an a-grain or a c-grain. The resulting data point in a map would indicate a region consisting either of pure c or pure a-axis oriented grains, which would be a wrong representation of the area. Instead, if the spot size is of the same size as the area it represents, the resulting Raman signal would be a wreighted average of all features detected in the area.



Figure 18. Spatial map of an a-axis oriented grains embedded in a c-axis oriented matrix. (b) REBCO tape with a-axis grain oriented.

On the other hand, the ability of resolve spectral features and bands into their separate components is known as spectral resolution. This feature is defined by the focal length of the spectrometer and number of grooves in the grating. The focus plays and important role in spectral resolution, where in a production line the focusing can change as a tape passes under the Raman characterization station. The tape can have surface changes such as topography, loss of flatness, vibration, etc. Typically, low to medium resolution is employed for basic chemical identification and pronounced changes on the microstructure. And high resolution is preferred when possible subtle changes of spectral features are prompted to occur. Therefore, in this study the effect of defocus as well as surface variation were investigated. Figure 19 shows the effect of defocus on Raman spectra when a confocal hole is used in addition defocus manually generated in z axis. The parameters were kept at 2 second acquisition time, 1.25 mW laser power, x50 magnification lens with 0.75 NA, and the defocus ranging from zero for the tape in focus to 30 microns with 2 microns step increments. The results showed that under the mentioned experimental conditions a defocus of 10 microns is estimated as maximum acceptable to keep an admissible SNR of the Raman spectrum. Additionally, from Figure 19 is clear the drop on the spectrum intensity from focus (brown line) to 10 microns defocus (blue line), which is an important result to pay attention in order to erroneously interpret it as a real drop due to changes on material structure instead of simply defocus. Therefore, regarding the results obtained for these specific settings, a defocus greater than 10 microns is not recommended. However, it could be improved by increasing the confocal hole size or removing it completely or by increasing the acquisition time.



Figure 19. Defocus effect on spectral resolution for acquisition time of 2 second and defocus ranging from 0 to 30 microns.

Consequently, to analyze the effect of acquisition time when defocus is carried out, the same experiment was conducted for an acquisition time of 10s. The results are shown in Figure 20 is clear the collection time plays an important role inclusive when defocus is induced allowing acquisition of strong signal. Figure 20 (a) shows the raw data where the spectral resolution is high even when the sample has been defocused 30 microns away from focus plane. Now in order to analyze if there is a change on peaks ratios when defocus occurred that may mislead the interpretation of results, the spectra were normalized as shown in Figure 20 (b) and clearly no changes in peak ratios are observed for any of the defocus conditions. In the case of 30 microns defocus, an increase of the background is seen but in overall the same trend is followed.

Yet, for a reel-to-reel system for analysis of long tapes the acquisition time must be limited to few seconds and ideally milliseconds to achieve ideal scanning speeds for industrial set ups.



Figure 20. Defocus effect on spectral resolution for acquisition time of 10 seconds and defocus ranging from 0 to 30 microns. (a) Raw plots. (b) Normalized plots

4.2. Data Processing

After analyzing the main factors that contributes to Raman spectra acquisition and deciding the optimum parameters for Raman mapping, data processing is utilized with the purpose of removing cosmic rays, dark noises, spectral artifacts, background subtraction, fluorescence, or any useless signal that may lead to misinterpretation of the results. In this subsection the treatment of the acquired data will be presented.

4.2.1. Cosmic Rays Removal

Cosmic rays are high energy radiation that randomly happens and can disturb the final Raman spectra by the emergence of cosmic spikes which are not related to samples characteristics. The

occurrence of these comics rays is unavoidable specially when long acquisitions times are selected. These spikes can be considered as false positive at the first sight; however, they are distinguishable from real samples Raman bands when study in detail. Therefore, to avoid misleading on the interpretation of Raman measurements the first step on data processing is cosmic rays' removal. In this study, an automated code to detect and remove high intensity spikes 'cosmic rays' have been developed, where the median and/or grub method is used during data processing.[91] Figure 21 shows the effectiveness of the automated code developed for cosmic rays removal.



Figure 21. Exemplification and effectiveness of cosmic ray removal by the code developed in this study. Raw data is presented by the red line while the corrected spectrum is shown by the blue line.

4.2.2. Background Calculation and Removal

Background is another important issue one have to deal with when interpreting Raman signal due to this is a strong effect in comparison with Raman effect that can overwhelm the final spectrum [46]. In addition, background makes peak analysis based on peak intensity ratios erroneous for a simple reason that if y_1 and y_2 are two real peak intensities, their ratio is y_1/y_2 , but in presence of background b, the perceived peak ratio would be $(y_1+b)/(y_2+b)$. If we take a simple illustrative case where $y_1=3$, $y_2=1$, b=4, then the real peak ratio is $y_1/y_2=3$ but the perceived peak ratio is $(y_1+b)/(y_2+b) = 7/5 = 1.4$.

The background profile mainly depends on sample characteristics as some can be more prompt to fluorescence when interacting with Laser. Also, higher laser wavelength contributes to higher background, as well as optics and pinholes also contributes to changing detected background. [73] An automated code based on an adaptive rolling ball for baseline subtraction has been developed in this study, which has demonstrated high robustness and capability when handling data with higher backgrounds as shown in Figure 22, where the code was implemented for subtraction of background when using a 532 nm and 638 nm laser, proving high accuracy of background subtraction. The rolling ball approach is equivalent to top hat filtering with a circular structuring element.



Figure 22. Exemplification of the processed data after background subtraction for lasers 532 nm and 638 nm. It is demonstrated the developed code has high robustness and is capable to intervene different spectra.

4.2.3. Raman Peak fitting

In order to correctly interpret Raman spectra, it becomes necessary to precisely fit the peaks intensity and shape specially when overlapping can occur such as the case for REBCO tapes. There are different mathematical models that can be implemented for peak fitting. In our case for peak fitting, we use either a Voight or Pseudo-Voight, which has shown high accuracy and reliability. This method consists of constraining non-linear minimization of the objective square norm of the overall error function between the background and cosmic ray subtracted data. The resulting curve is a collection of all the fit peaks from addition of all fitted peaks. In Figure 23 is presented an example of the effective peak fitting processing using a real spectrum, where original data is represented by the dash blue line and peaks fit by red lines. The integrated spectrum after data processing is shown by the continuum black line.



Figure 23. Illustration of peak fitting obtained by the automated coded developed. The scattered points in blue represented the raw data, and the red peaks are the individual peak fits. The black line is the integrated spectra from all the peaks that were fit.

With the purpose of testing the effectiveness and robustness of the developed code, this we used to process collected data from different materials. Figure 24 compares the spectrum of two samples deposited on silicon substrate by implementing the code developed in this thesis. Figure 24(a) is a carbon-based sample and Figure 24(b) is a silicon-carbon based thin films. In this study, a 532 nm laser and a x100 magnification lens used. In both cases, high quality of the data was achieved demonstrating the automated code is satisfactory and accurate for a variety of materials, laser wavelengths, and background signals.



Figure 24. Evaluation of the automated code developed for data treatment, using a 532 nm laser. (a) carbon-based sample. (b) Silicon-carbon base thin film.

4.2.4. Surface Topography Sensitivity

For Raman measurements a special sample preparation is not required, however, keeping a flat surface is crucial to avoid out of focus signal and inconsistent intensity. During this experiment, the tendency of some tapes to curve is higher from one to another, depending on sample thickness, where thicker samples generally result in more curling and thus loss of intensity of characteristic peaks. Therefore, sample handling also plays a critical role in the signal throughput. For this study, the flatness of the sample was corrected and a strong grip on the sample was obtained by using a double-sided tape 'Z-Tape' (Ted Pella Inc.) in addition to press leveling (see Figure 25). Shown in Figure 25 (a) is the sample held by a common double sided scotch tape, where the poor grip of the tape and the tendency of the sample to curl is evident. In addition, the Raman map taken from this sample shows the detrimental effects of the low flatness of this sample leading to uneven and unsatisfactory results. Effectively, tape curl is in most ways identical to the defocus effect, which is particularly pronounced when using confocal

Raman, which is the case in this study. On the other hand, shown in Figure 25 (c) is the sample held by a double sided Z-Tape, where it is clear that the Z-Tape can achieve strong grip and thus flatness of the sample, resulting in favorable response for the acquisition of the it respective Raman map, where the signal/background ratio maintains constant value across the analyzed area.



Figure 25. Set up used to improve flatness of the tape. (a) Tape held by regular double sized Scotch tape and its respective Raman map of 225 collected spectra. (b) Press leveling utilized to achieved press the tape to achieve maximum grip. (c) Tape held by Z-Tape (Ted Pella Inc.). Flatness of the tape is ensured, even after many days of being released from the press leveling, and the Raman map of 225 points acquired for this sample.

The effect of loose sample in comparison with strong grip is presented in Figure 26 where the integrated Raman spectra for 441 scans obtained is displayed in addition to their scanned maps normalized to peak at $146 \ cm^{-1}$. Here, the term loose sample refers to the sample held by

regular double sided Scotch tape which is prone to debonding from the sample. Z measurements correspond to the samples held by the Z-tape and measurement 1 has been done immediately after being released from the leveling press while measurement 2 is a repeated measurement over the same area after the sample has been left on the system overnight. The two measurements were conducted to prove the grip quality of the tape and to see possible variation of sample curvature. Figure 26 (a) shows the integrated spectra obtained for the same sample under different flatness conditions. The black line represents the loose sample. In this spectrum the shift of the peaks to lower frequencies and diminishes of the average intensity is observed if compared to well held samples, showed by gray and red lines, where more resolved peaks, and almost same peaks intensity and position are maintained. The shift on wavelength seen from loose to well secured samples clearly might lead to wrong interpretation. Figure 26 (b) is the intensity map of the loose sample. The intensity varies smoothly, and the observed image resembles the curled tape. Figure 26 (c) and Figure 26 (d) are the intensity map for pressed sampled samples after released from mechanical pressure and after 12h of the first measurement, respectively. The two maps look very similar regarding intensity over the entire area, proving there is no loss of flatness between the measurements. This study demonstrated the importance of having excellent flatness of the sample to obtained precise information of the investigated samples.



Figure 26. Effect of efficient flatness of a sample using a Z-tape on integrated spectra of 441 points. (a) Black line is the integrate spectra for 'Loose sample' grip with double sided Scotch tape. The red and gray line are the spectra for well held samples using the Z-tape but with a difference in measurement day of 2 days. (b) The intensity map recorded for the "Loose sample". (c) The intensity map for Z tape measurement 1 after being pressed 12h and (d) The intensity map for Z tape measurement 2 after 24h of being release from the press leveling.

4.3. Scanning of Defective REBCO Tapes

In this section, the performance of Raman scanning after optimization of system parameters will be evaluated over samples with defective regions that showed significant dropouts in critical current. The purpose of this experiment is to find possible reasons at the structural level that lead to the loss in superconducting properties and demonstrate the advantages of implementing Raman spectroscopy over conventional methods such as 2D-XRD. Therefore, to compare these two methods, 2D-XRD linear maps of the defective regions have also been measured and will be presented.

A preliminary analysis on samples with heavy defects was conducted to prove the high performance of the Raman system for the selected parameters in this thesis. Figure 27 shows a photograph of the defected sample with the scanned map of 2.4x3mm of a REBCO tape. This is a wavelength map, rather than intensity map. There are 17 identified peaks identified, however in the current figure only the peak with the average wavelength of $129 \, cm^{-1}$ associated to (Cu_2) mode is shown for illustration purposes.



Figure 27. Heavily defective REBCO tape. (a) The photograph of a defective sample with a wavelength map on top where the map was acquired. (b) Corresponds to the zoomed area where the map was taken. In this inset the variation on tapes color concur with the drastic change on wavelength seen in the map by the change in color.

The examination of the tape by scanning Raman shows an excellent agreement with the Raman shift. The change in map color indicates the shift of the peak, which also corresponds to the change on tape contrast. Figure 28. is an extended map taken from the same tape but scanning a greater area; Figure 28(a) is the wavelength map normalized to the peak 529 cm^{-1} . Figure 28 (b) shows the intensity map normalized to the 126 cm^{-1} peak. From the region scanned on this sample, it is clear the abrupt change on wavelength and intensity, from this experiment we can conclude that the parameters selected have a great level of spatial resolution and spectral resolution for detection of defects and nonuniformities. These two figures were presented to

demonstrate the capabilities of scanning Raman on detection of difficult areas on REBCO tapes. Following this experiment, the actual study on defective REBCO tapes with critical current dropouts is presented.



Figure 28. Raman map over and extended area. (a) Raman wavelength of 126 cm^{-1} peak. (b) Raman intensity map of 585 cm⁻¹ peak. The inhomogeneity of the sample is clearly captured by these scanning maps.

4.3.1. Raman Scanning Measurements of Defective Tapes

Figure 29 shows another Raman map of a defective region. Shown in Figure 29(a) is the Raman map of the 330 cm^{-1} peak intensity which is attributed to (O_{2+}/O_{3-}) out-of-phase mode characteristic of c-axis oriented grains and is supposed to be predominant for well texture REBCO films [92, 93]. This map is overlapped on a photograph of the defective sample, and it covers most of the 12 mm of tape width and its dimensions concur with the labeled x and y

axes, respectively. The corresponding Raman spectra for this map in shown in Figure 29(b), which are integrated spectra representative of subareas labeled with the x and y axis integration ranges; clearly the results reveal significant variation in the spectral features for each subregion.



Figure 29. Raman map and the integrated Raman spectra (a) Raman map of the scanned area, showing the intensity of the O2+/O3- peak nominally at 330 cm-1. (b) Integrated Raman spectra from selected subareas.

The drop out in the critical current (I_c) measured by Scanning Hall Probe Microscopy (SHPM), was reported around 55% lower relative to the region free of defects, which has an I_c of 425 A/12 mm width. The defective regions in this sample are located at the bottom and top along the y direction. The integrated subareas where of 2x2 mm at y = 0.5-2.5mm, y = 5-7mm, and y = 8.5-10.5mm, changes are observed not only for (O_{2+}/O_{3-}) peak, but also for (Cu_2), (O_4) and cation disorder (C-dir) mode, confirming the inhomogeneity of the investigated sample at these three locations.

Raman active modes observed on our REBCO tapes are limited to the range of 130 to 700 cm^{-1} , giving priority to the well understood first order Raman active modes established in the literature. Theses samples are believed to be well-oxygenated. Therefore, an orthorhombic structure is assumed, where the (O_{2+}/O_{3-}) and (O_4) modes have been related to superconducting properties [92, 94, 95] and they are expected to be at maximum intensity for (O_{2+}/O_{3-}) at 330 cm^{-1} while (O_4) mode at 500 cm^{-1} should be at its minimum intensity or absent. Otherwise, presence of (O_4) mode indicates a-axis grains or c-axis tilted grains orientation, which can be detrimental for the superconducting properties. From the three subregions analyzed from the map, the well-textured c-axis oriented structure is found between y = 2-8 mm, and a region with remarkable presence of cation disorder peak, represented by the mode at 600 cm^{-1} , is visible between y = 4-6 mm, and above y = 8 mm purely a-grain oriented REBCO is observed. Finally, in the region below y = 2 mm, the intensity signatures of (Cu_2) and (O_{2+}/O_{3-}) and even cation disorder are similar to the top region y > 8 mm.



Figure 30. Raman scanning maps for wavelength shift and intensity variation of Cu_2 , O_{2+}/O_{3-} , O_4 , C-dis.

Shown in Figure 30 are the maps normalized to the peak intensity and wavelength of (Cu_2) , (O_{2+}/O_{3-}) , (O_4) and C-dir modes for the same examined region as shown in Figure 29 (b). Presented in this figure at the top and bottom rows are maps of wavelengths and intensities, respectively, as determined from Voigt peak fits. These maps clearly reveal the great level of detail regarding c-grain, a-grain, and cation disorder as a function of location. For example, the wavelength maps could be used as a reference for structural disorder from the frequency of C-dis modes, or oxygen content using the frequency of (O_4) [14]. The Raman spectrum along the y axis is shown in Figure 31 (a). Besides in Figure 31 (b) the extent at which the transition from c-axis to a-axis oriented region occurred is shown. In Figure 31 (c) an inset of the (O_{2+}/O_{3-}) peak is zoomed, where one can observe a significant weakening of this peak when

reaching y = 8.4 mm. Most of the bands reduce the intensity strength while the ~500cm⁻¹ (O_4) mode increases in intensity at y = 10.2 mm. At this location, the higher intensity of the (O_4) peak combined with the decline of the intensity of the other peaks cannot be explained as a consequence of oxygen deficiency mainly because a shift to lower frequencies is not observed, but rather it is the result of a change in grain orientation to a-axis oriented grains.



Figure 31. (a) Sequential Raman spectra along y axis in 2 mm increments and x = 5 mm. (b) Integrated Raman spectra for y range of 6.8-8.8 mm to reveal the width of the transition region from c-axis to a-axis oriented grains. (c) intensity of Raman O_{2+}/O_{3-} peak in the same transition region.

The Raman scanning method implemented in this thesis has proven to be very informative in terms of the sample structure, demonstrating its feasibility for being implemented in a reel-toreel quality control system. With the intention of increasing the worth of this technique another example is presented in Figure 32. This figure shows the map regarding wavelength and intensity of the (O_{2+}/O_{3-}) mode. The integrated spectra for regions at y = 2-3 mm, y = 5-7 mm, and y = 9-11 mm are shown. From these measurements a strong presence of the cation disorder band is evidenced from 2 mm to 7 mm approximately, which differs from the sample analyzed above where this strong band was only observed between 5 mm to 7 mm. On the other hand, a small increment on (O_4) mode intensity is seen at 9-11 mm range. This feature is not strong enough to determine if the changes are solely attributed to pure a-axis grains orientated as suggested on previous sample (Figure 29). Finally, the wavelength map shows a shift of this peak to higher frequencies in the bottom region at y = 2.6 mm and y = 10-11 mm. This could be attributed to subtle changes on oxygen content, transforming the structure from orthorhombic to tetragonal or any middle state like ortho-I or ortho-II domains [71, 96]. For comparison purpose, one additional example of Raman mapping on defected areas are presented in Appendix A, and one example for mapping of different materials is shown in Appendix B.

Raman scanning on defected areas has demonstrated suitable for analyzing REBCO thin films along greater areas, which is valuable for in application on quality control of long length conductors.



Figure 32. Illustration of a scanning map run in a different sample, where evolution of the O_4 peak is not as strong as observed in Figure 29, instead C-dir band is strong along 2-7mm.

4.3.2. 2D-XRD Scanning Measurements

With the intention of demonstrating the potential of Raman as a more reliable characterization and quality control method, a 2D-XRD linear map along y with 0.5mm steps from point to point were taken. In Figure 33 the scans corresponding to y = 2mm, y = 6mm, and y = 10mm are presented, which were selected to be compared with the subregion evaluated by Raman scanning. From the 2D-XRD measurements, it becomes clear that the region at y = 10 mmconsists mostly of a-grains also visible by the integrated Raman spectrum in Figure 29 (b) at y = 8.5-10.5mm, where the dominant peak is for (O_4) mode attributed to presence of a-axis grains oriented [92] in addition to the inhibition of the (O_{2+}/O_{3-}).

Raman measurements as well as 2D-XRD results showed strong agreement regarding the features found at the top of the samples where the structure was mainly a-axis grains, however, the results at the bottom has not such agreement. The 2D-XRD map is near identical for the bottom and middle region in comparison with Raman spectra where the changes are distinguishable between the two regions. It is worthy to mention, that while Raman mapping give a result of an average area, 2D-XRD only offers information of a specific point, which can be a reason why it could not detect the subtle changes at the lower area.



Figure 33. Diffraction patterns from three selected points along the y axis.

The corresponding XRD spectra obtained from integration of 2D-XRD scans around 00L peaks are shown in Figure 34, which confirm presence of the a-axis oriented region as shown in Figure 29 (a) at about the same location. In Figure 34 (b) is shown the XRD peak transition from REBCO (006) to REBCO (200) along the "y" direction revealing the film orientation change from c-axis to a-axis grains. The transition is also illustrated in Figure 34 (c), showing the integrated intensity of REBCO (005) c-axis oriented and REBCO (102) a-axis oriented peaks along "y" location. These results clearly indicate a transition to near-pure a-axis grain for y > 8 mm and c-axis grains texture for y below \approx 8 mm. We note the band regarding cation disorder observed by Raman spectroscopy as its variation along "y" is not readily observed by XRD reflections nor original 2D-XRD scans.



Figure 34. (a) X-ray diffraction pattern of REBCO superconductor tape for different positions on y axis, and x-axis fixed at 5mm. (b) Peaks zoomed, show the transition of c-grains to a-grains (c) XRD planes of 005-c grains, and 102-a grains as a function of Y position.

Figure 35 (a) presents a comparison between a new segment of defective tape, where the appearance of the defect has a narrow vertical line that varies along the length unlike the observed in previous cases where the defect varies along the width. The dropout in critical current detected by SHPM is only $\approx 15\%$ relative to the baseline of 120 A/12 mm width. In
Figure 35 (a) is provided the Raman scanning map normalized to the intensity of the O_4 , which is pronounced at the defect region. The corresponding 2D-XRD result is shown in Figure 35 (b), where the observed patterns represent the defect-free region to the left at x = 24.1 mm and the defect region to the right at x = 29.6 mm. It is noteworthy to elucidate the defect seen on Figure 35 (a) is not related to a-axis grains texture, instead it is due to slightly out-of-plane caxis oriented grains. This effect is also confirmed by the streaking of (00L) and (10L) peaks detected by 2D-XRD (see Figure 35 (b)). Raman prove is potential to not only detect severe defect as previously shown but also slight changes on the film texture.



Figure 35. (a) Raman scanning map of the intensity of the O_4 peak characteristic of tilted grains for an area of 12x4mm. (b) 2D-XRD diffraction pattern of two locations, y = 5 mm, x = 24.1and 29.6 mm. The patterns reveal variation in the degree of out-of-plane texture of the film due to the presence of the defect, consistent with the O_4 map.

4.4. Polarized Raman Spectroscopy for Texture Analysis

The effect of REBCO crystal orientation on Raman spectra has been studied in depth by several groups [94, 97-102], which have demonstrated the capability of Raman spectroscopy to quantify not only out-of-plane but also in-plane texture. Therefore, polarized Raman has been carried out to quantitatively determine the uniaxial and biaxial texture of REBCO tapes. The uniaxial texture can be resolved by the fraction of out-of-plane c-axis grains, which is calculated from the ratio between $I_{o_{2+}/o_{3-}}$ and I_{o_4} and is denoted by the parameter (δ). The biaxial texture on the other hand is complemented by measuring the in-plane orientation (a-b plane) and is calculated by the intensity of Raman modes when the sample is rotated about the z-axis \perp to the film surface. For this analysis, Raman measurements are compared to XRD φ -scan results to show the relationship between XRD- φ -scan and Raman measurements for texture determination.

The angle of misorientation of the YBCO grains is an important factor related to the drop of the critical current. Consequently, knowledge of the crystal texture leads to a more precise understanding of the material properties, where well oriented c-axis grains (out-of-plane) and ab-axis grains (in-plane) are desired to determine high texture crystals. Pratap et al, had found a good correlation on critical current and crystal texture when ϕ -scan FWHM values are below 2.35° and 1.25° for in-plane and out-of-plane texture, respectively. [103] In this section, the potentiality of polarized Raman for local analysis of the texture uniformity of REBCO samples is presented.

Two REBCO samples characterized by ϕ -scan FWHM with 4.75° and 5.65° values of in-plane texture were analyzed by polarized Raman. The spectra were recorded in backscattering

geometry, as it has been explained in chapter 2, using the Porton notation to identify the polarized $z(x, x)\overline{z}$ and depolarized $z(x, y)\overline{z}$ configuration. The following results are obtained utilizing the formulas and Raman tensor values for $X_{Ag}^2 = Y_A^2 = 2$, $X_{B1g}^2 = Y_{B1g}^2 = 8.5$, and $Z_{Ag}^2 = 100$, from the method determined by ref [97, 98] for convenience. However, we note that the film in this study contains a 50:50 mol.% mixture of RE elements Gd and Y instead of pure Y, as well as addition of Zr forming BZO nanorods, which may affect the actual values. The results are divided into; the uniaxial analysis, which corresponds to the c-fraction (out of plane) texture parameter (δ), and the in-plane orientation parameter (Q_c), and the biaxial texture is determined from parameters obtained from c-fraction and in-plane orientation δ and Q_c , respectively.

4.4.1. Uniaxial Texture c-fraction (out-of-plane)

The c-fraction texture parameter δ is obtained from equation (10) considering the Raman tensor mentioned above. The "r" parameter is calculated from the ratio between the intensity c-grains and a-grains using equation (11), where I_c and I_a are the sum of integrated intensity of c-grains (O_{2+}/O_{3-}) mode and a-grains (O_4) mode from polarized and depolarized spectra. Therefore, the delta parameter (δ) defines the c-axis grain fraction texture, where δ close to 1 indicates good out-of-plane texture and zero for in-plane orientation.

$$\delta = \frac{r \left(Z_{Ag}^2 + X_{Ag}^2 \right) - X_{B1g}^2}{r \left(Z_{Ag}^2 - X_{Ag}^2 \right) + X_{B1g}^2}$$
(10)

$$r = \frac{I_c}{I_a} = \frac{I_c^d + I_c^p}{I_a^d + I_a^p}$$
(11)

Where I_a^p and I_c^p are the polarized intensity for a-axis and c-axis grains, I_a^d and I_c^d are the depolarized intensity for a-axis and c-axis grains.

In Figure 36 the spectra for polarized and depolarized Raman are presented for both samples. When the laser beam hits perpendicular to the tape surface under polarized configuration $z(x, x)\overline{z}$ the Raman intensities expected is higher for (O_{2+}/O_{3-}) and very low for (O_4) mode. In the case of depolarized geometry $z(x, y)\overline{z}$ no relative intensity is expected to be seen. [104] Therefore, from equation 9 the values obtained for sample one and two are $\delta = 0.9586$ and $\delta = 0.9681$, respectively, which indicate almost a perfect c-axis oriented film.



Figure 36. Polarized and depolarized Raman spectra for two REBCO A-MOCVD samples.

In Figure 37, the uniaxial textured factor δ determined by Raman measurement is presented as a function of the FWHM ϕ – scans for both samples investigated. From this figure no relation between the degree of in-plane texture found by FWHM ϕ -scans shows correlation with c-fraction parameter, as also has been found by Gonzales et al. [98] Consequently, δ parameter

only offers information regarding the c-axis well-oriented grains. The c-fraction values determined were above 0.9 for both samples, which indicates low or absence growth of a-axis grains.



Figure 37. Fraction of c-axis oriented crystal from Raman measurements as a function of the biaxial texture measured by FWHM ϕ -scan.

In order to examine the Raman performance regarding the crystalline texture, the parameter δ has been determine for the defected samples presented in section 4.3. the same Raman tensor values have been used here. The resulting map as a function of δ parameter indicating the c-axis oriented grains is shown in Figure 38 (a), and its corresponding linear map along y direction is presented on Figure 38 (b), where the red line is the average along the "x" direction of the respective map for different locations along the "y" direction. The black line on the other hand, is the integrated intensities of REBCO (005) c-axis oriented peaks obtained by 2D-XRD scan, which is used for direct comparison with c-fraction parameter.



Figure 38. (a) Raman map of δ function [98], as calculated from O_{2+}/O_{3-} and O_4 maps, indicating fraction of c-axis oriented grains. (b) Integrated δ function as a function of y position (red) and normalized intensity of REBCO (005) peak obtained from 2D-XRD scans.

From Figure 38 (b), a very good agreement between the Raman δ and 2D-XRD measurements can be observed. First, the positional consistency of the transition from the c-axis to a-axis oriented region between the two techniques is evident at y = 8 mm. Second, the subtle change in REBCO (005) intensity in the y = 0.5-2 mm region is also detected by Raman spectroscopy, as can be seen not only from the averaged linear map in Figure 38 (b) but also from the subtle color change in the 2D map in Figure 38 (a), corresponding to δ ranging from ~0.9 to ~1 in the lowest region of the map. In the a-axis region (y > 8 mm), Raman δ does not decrease to nearzero as the 2D-XRD map suggests. This aspect may stem from residual noise in the map, potentially different Raman tensor elements in the film compared to the values used in the calculation, as discussed earlier, or other factors. Another possible cause if the fact that values obtained from O_{2+}/O_{3-} and O_4 mode were taken by unpolarized Raman, which means not polarizers are used then light is collected from all directions, maybe this can be the reason why sensitivity to c-fraction detention is lower in comparison to XRD measurements. However, and very remarkable is that even when unpolarized light is utilized as in this case, reliable information is achievable. As a result, lower acquisition times for the same measurements from Raman mapping can be used to determine the c-fraction, in addition no other techniques such as 2D-XRD are required to be performed to study the c-axis texture.

4.4.2. Biaxial Texture (in-plane orientation)

The degree of in-plane orientation by using polarized Raman can be found by rotation of the angle φ between the incident laser and the cristallografic axes of the film. For this analysis, two angle positions were employed at $\varphi = 0^{\circ}$ and $\varphi = 45^{\circ}$ to clarify this study for only two angles was realized with the purpose of proving Raman capabilities for investigating the in-plane texture. However, for very precise results more angles should be used. In addition, this experiment was conducted utilizing polarized and depolarized configurations.

Gonzalez et al. [98] have developed a simple method to determine the in-plane texture, where the texture parameter "Qc" can be determined from equation (12), where the k_1 and k_2 values are found through the numerical fit from the experimental Raman data to a distribution function. The k_1 parameter in dependent on the rotational angle and k_2 is independent. Consequently, an excellent in-plane texture is found when the Qc parameter is close to 1 and a poor texture close to 0. [56]. The delta parameter is the same value found for c-fraction above.

$$Q_c = \frac{k_1}{4A\delta x_{B_{1g}}^2} = \frac{k_1}{k_1 + 8k_2} = \frac{\frac{k_1}{k_2}}{\frac{k_1}{k_2} + 8}$$
(12)

To simplify the above equation, Qc was solved as a function of k_1/k_2 ratio, which allows to eliminate contribution from system issues, actual Raman tensor values, and integration time, among others. The k_1 and k_2 values for depolarized and polarized Raman measurements can be obtained from the equations (13) and (14), respectively:

$$I_{B_{1g}}^d(\varphi) = k_1 \sin^2 \varphi \cos^2 \varphi + k_2 \tag{13}$$

$$I_{B_{1g}}^{p} = \frac{1}{4}k_{1}(\sin^{2}\varphi - \cos^{2}\varphi)^{2} + k_{2}$$
(14)

The I^{d}_{B1g} and I^{p}_{B1g} correspond to the integrated intensity from polarized and depolarized measurements. According to Gonzales et al. it is not highly necessary to use the spectra of polarized and depolarized light for calculation of Q_c parameter as they have found that the obtained results are relatively similar, in addition to is simpler to use depolarized than polarized geometry where for the former polarization leakage or calibration issues can be a factor that may affect final results. [102] Therefore, this group recommends that only depolarized Raman must be analyzed. [56]

Table 5 shows a compilation of values found for Q_c , k_1 and k_2 in additon to the ϕ -scan FWHM values obtained by XRD measurements. The values acquired after using equation 11 shows that as the value of ϕ -scan increases the Qc decreases, indicating that sample M-300-2 has a better in-plane texture than M-300-6. The values obtained through polarized Raman are in good

agreement with the results found through full width at half maximum (FWHM) x-ray ϕ -scan method, where sample M-300-2 presented a better in-plane orientation than M-300-6.

Samples	M-300-2	M-300-6
φ-scan FWHM	4.75°	5.65°
Q _c in-plane	0.88	0.86
k ₁	212.19	74.90
k ₂	4.46	1.54

Table 5. Qc parameter and k_1 , k_2 values obtained from fitting equation (12).

In Figure 39 the Q_c parameter in function ϕ -scan FWHM is presented. The Q_c parameter decays when the misorientation angle increases. The results indicate the Q_c parameter can be measured quantitatively using micro-Raman as well as x-ray ϕ -scan, achieving a good representation of the biaxial texture of REBCO thin films. However, it needs to be noted that to perform this analysis, polarized light has to be used and the sample has to be rotated about the axis \perp to the film surface, which for reel-to-reel applications utilizing stationary Raman system and moving tape can become a problem as the long tapes are limited to x – axis movement. However, an implementation of a customized Raman system, e.g., fiber Raman probe or automated rotary polarizer, can readily accommodate any incident beam rotation.



Figure 39. Experimental Q_c values as a function of the rotation angle.

In the light of this experiment, Raman spectroscopy has proven to be a powerful method for biaxial texture analysis and can offer plenty of information of the epitaxial quality of the investigated samples. We note the polarization test was performed in collaboration with Dr. V. G. Hadjiev.

4.5. Correlation studies

The following study was performed in light of correlating Raman measurements and in-field performance of 45 samples. Those samples have different amounts of Ba, as well as Zr and Hf as doping elements for formation of nanorods. The Ba is added as alloying element, while Zr and Hf additions are only dopants. The intention is to improve REBCO coated conductor (CC) superconducting properties. The objective of this analysis is to correlate Raman peak wavelength and Raman peak intensity to critical current density (J_c). There are 17 peaks observed on a spectral range of 132 cm^{-1} to 1650 cm^{-1} . The (J_c) was measured in magnetic

fields varying from 0 and 14T at temperatures of 4.2, 20, 30, 40, 65, 77K. The main goal of this study is to find whether Raman features can predict changes in terms of critical current performance at different magnetic fields and temperatures.

The databases acquired for the 45 samples consist of scanning Raman maps of an area about 1x1mm containing 225 spectra per sample, where the integrated spectrum will be used as an average representation. Samples are also characterized by Vibrating sample magnetometry (VSM) with magnetic fields between 0-14 T and six temperatures at 4.2, 20, 30, 40, 65, 77 K. In addition to the correlation of the Raman features to in-field performance, we also make the assessment to unit cell composition obtained by ICP and WDS methods as a function of in-field performance and Raman measurements will be revised. We note this analysis lies on a statistical viewpoint rather than an existing physical model.

Pearson's correlation coefficient has been used to measure the strength of the linear relationship of the above-mentioned variables using equation (5) presented in section 2.5.1. A significant correlation has been set for a p-value lower or equal to the significance level $\alpha = 0.05$. We note the confidence limit for industrial applications should be lower than $\alpha = 0.05$. The degree of correlation has been established by some authors as shown in Table 6 [105].

Very High Correlation	$\rho = \mp 0.9 \text{ and } \mp 1$
High Correlation	$\rho = \mp 0.7$ and ∓ 0.89
Moderate Correlation	$\rho = \mp 0.5 \text{ and } \mp 0.69$
Low Correlation	$\rho = \mp 0.30 \text{ and } \mp 0.49$
Very Low or Any Correlation	$\rho = 0$ and ∓ 0.29

Table 6. Degree of correlation [105]

Shown in Figure 40 is a plot of Pearson's correlation between Raman peaks intensity (y axis) and critical current density (J_c) x – axis as a function of magnetic field 0-14T for each temperature 4.2, 20, 30, 40, 65, 77K. For clear understanding of the graphs according to the significance level selected, no correlation is represented by zero values or green color. Additionally, from the map two interpretations of the results can be drawn, the sign of Pearson correlation coefficient gives the direction of the relationship between the variables, where negative sign indicates negative correlation as one variable increases the other decreases or vice versa. In the case of a positive sign the relation between the variables is to increase together. Finally, from the y-axis some of the peaks have been identified as found in the literature for REBCO thin films as mentioned in previous chapters such as C-dis have been related to addition or substitution by foreign elements, O_{2+}/O_{3-} and O_4 attributed to superconducting properties, among others.



Figure 40. Significant correlation between Raman peak intensity and critical current density (J_c) as determine by VSM measurements.

The results observed in Figure 40 indicates that a significant number of peaks (7-8) as a function of intensity show significant correlation with in-field performance. For example, Figure 41 shows an inset of the correlation of the peak 600 cm⁻¹ as a function of critical current at 12T and 65K where the correlation coefficient is 0.57 which indicates a positive correlation as the intensity of this peak increases the critical current density increases as well.



Figure 41. Correlation coefficient peak 600 cm⁻¹ as a function of 12T and 65K, it is an inset from the correlation map Raman Intensity vs J_c .

On the other hand, there is a moderate negative correlation for peak at 792 cm^{-1} , which indicates as the intensity of the peak increases the critical current density drops, this is seen for all six temperatures for fields higher to 3T. Also, for the 502 cm^{-1} peak, there is a low negative correlation about -0.4 for self-field. In Figure 42 the correlation plot between Raman peaks wavelength and critical current is presented, where a moderate negative correlation about -0.6

is observed for peaks at 331 cm^{-1} and 391 cm^{-1} . Considering O_{2+}/O_{3-} peak frequency at 331 cm^{-1} is characteristic of orthorhombic superconducting phase, this plot indicates that as the frequency of the this peak increases, which corresponds to tetragonal or intermediate phases, the critical current density (J_c) drops suggesting loss of the superconducting characteristics.



Figure 42. Correlation coefficient between Raman peak wavelength and critical current density (J_c) .

In Figure 43 an inset corresponding to peak $331 \ cm^{-1}$ at 65K and 13T from correlation map of Figure 42 is presented, which is a negative correlation of -0.61, indicating that as the peak shift to higher frequencies then the critical current density decreases. Overall, for the 45 samples analyzed, not all Raman features seem to correlate with superconducting performance. However, it is noteworthy that as proof of concept the correlation found for some of these

Raman features is remarkable and entitles deeper research. We recommend for future work to increase the number of samples and develop specific protocols that allow higher accuracy on samples data acquisition.

An interesting remark from this correlation study is that the well-known Raman bands O_{2+}/O_{3-} , O_4 , related to superconducting properties, correlates not only with Raman intensity but also with Raman wavelength. The intensity of the Raman mode O_{2+}/O_{3-} show no correlation as a function of the critical current density, however it is observed a clear correlation regarding Raman wavelength vs (J_c) . The case for the increase of O_4 intensity correlates with the drops of J_c , which is a well understood behavior where the intensity increases due to the presence of tilted c-grains or a-axis oriented grains resulting in the deterioration of the superconducting properties of the material. Therefore, according to the correlation observed in Figure 40 the higher the intensity of O_4 Raman mode the lower the J_c , particularly at low fields and it is almost independent of temperature. Additionally, the cation and oxygen disorder modes also seen to have a certain positive correlation at higher fields for each temperature, since the increase in the intensity of this mode correlates with improvement in J_c .



Figure 43. correlation coefficient as a function of Raman peak wavelength at 13T and 65K.

Next, we evaluate the elemental composition obtained by WDS and ICP correlation with the in-field performance. Only 34 of 45 samples received for Raman analysis were also subjected to composition analysis by ICP, and for those samples WDS was carried out in this present study for comparison purposes. WDS was selected instead of EDS because of it is more precise which is an important requirement for this study. The correlation of composition as a function of in-field performance was performed using the unit cell values that have been obtained from the raw results using the equations outlined below. The minimum number of unit cell to form a REBCO structure can be found by equation (15).

$$REBCO_{uc} = min\left(RE, \frac{Ba_r}{2}, \frac{Cu}{3}\right)$$
(15)

Where RE are the rare earth elements used (Gd, Y), Ba_r is the barium residual after subtracting the doping element Zr for formation of BZO nanorods. The unit cells values for each element are obtained by diving by the *REBCO_{uc}* using equations (16-18)

$$RE_{uc} = \frac{RE}{REBCO_{uc}} \tag{16}$$

$$Ba_{uc} = \frac{Ba_r}{REBCO_{uc}} \tag{17}$$

$$Cu_{uc} = \frac{Cu}{REBCO_{uc}} \tag{18}$$

Finally, to calculate BZO and REO, the excess of Ba and RE is used as given in equations (19-24)

$$\Delta RE = \frac{RE - REBCO_{uc}}{REBCO_{uc}} \tag{19}$$

$$\Delta Ba = \frac{Ba_r - (2 * REBCO_{uc})}{REBCO_{uc}}$$
(20)

$$\Delta Cu = \frac{Cu - (3 * REBCO_{uc})}{REBCO_{uc}}$$
(21)

$$BZO_{nom} = \frac{Zr}{REBCO_{uc}}$$
(22)

$$BZO_{ex} = min(\Delta RE, \Delta Ba)$$
(23)

$$BZO = BZO_{nom} + BZO_{ex} \tag{24}$$

Where BZO $(BaZrO_3)$ are the nanorods introduced for improvement of superconducting performance, and REO (RE_2O_3) precipitates are determined by equation (25)

$$REO = \frac{\Delta RE - BZO_{ex}}{2}$$
(25)

Seen in Figure 44 and Figure 45 are the plots of correlation coefficient between the elemental compositional obtained from WDS and ICP methods as a function of the in-field performance at different temperatures and 0-14T fields. In these figures the composition is presented in unit cells, where the (Zr+Hf) factor is the sum of the doping elements added to the compound, dBaCu is the excess of either Ba or Cu in the compound as defined by equation (26), where a negative value indicates excess of Cu and a positive result indicates excess of Ba. The dBaCu*(Zr+Hf) is the factor of the excess of Ba or Cu multiply by the sum of doping elements.

$$dBaCu = (Ba_r - 2) - (Cu - 3)$$
(26)



Figure 44. Correlation coefficient plot of calculated composition from wavelength dispersive spectroscopy method as a function of the critical current density (J_c).

In Figure 44 a moderate correlation ≈ 0.5 of Ba unit cell is observed for fields 8-14T at 65-77K. Particularly, at 65K Ba shows high correlation ≈ 0.8 at 12-14T. At low fields 0-2T, Ba has a negative correlation at 65-77K. Overall, for temperatures 4.2 to 40K low correlation at 0-2T is only observed for Y, Gd, RE, and some for Cu at 65-77K. The Doping elements by their own does not follow a trend, but when together (Zr+Hf) a correlation from moderate to high is seen at 65 and 77K from 8-12T. Figure 45 presents the plot of elemental composition obtained by inductively coupled plasma atomic emission spectroscopy (ICP). The results obtained by using ICP strongly differs from WDS results, highlighting the important role of the precision factor if a comparison needs to be drawn. The only trend that can be observed from both plots is attributed to the doping elements factor (Zr+Hf), RE and Y at low fields. In ICP, Ba does not

show any correlation at higher fields as seen by WDS instead correlation at low fields for 20-77K is observed.



Figure 45. Correlation coefficient plot of calculated composition from inductively coupled plasma atomic method as a function of the critical current density (J_c) .

Shown in Figure 46 is the correlation coefficient of BZO and REO calculated from WDS as a function if in-field performance. REO have a low correlation for self-field at 40K and gets higher for self-field at 65 and 77K. It was found that these temperatures have a moderate negative correlation at fields greater than 8T. There is a moderate to high positive correlation for BZO at all temperatures at fields higher than 2T. This correlation gets higher at 65 and 77K in fields between 8 and 14T. Moderate negative correlation of BZO at 0-2T and 65-77K is observed, which may suggest that in self-field the less nanorods the better the critical current density (J_c).



Figure 46. Correlation coefficient plot between BZO and REO content from (WDS) and critical current density (J_c).

Figure 47 is the plot of correlation of BZO and REO as a function of ICP composition and infield performance. This plot in comparison to Figure 46 does not show any correlation regarding BZO; except for temperatures of 65 and 77k where one can see a low negative correlation. On the other hand, high correlation is seen for REO at all temperatures in the presence of low fields and gets stronger between 40 and 77K. This clearly shows remarkable differences between the results obtained by ICP and WDS. To note as found in the literature heavy doping (Zr) can improve superconducting performance especially at stronger fields. [106] It may suggest the trend observed from WDS data seems more accurate as it shows BZO (that forms by addition of Zr as doping element) having better correlation at higher fields that is not seen by ICP.



Figure 47. Correlation coefficient plot between BZO and REO content from (ICP) and critical current density (J_c)

Finally, plots presented in Figure 48 and Figure 49 correspond to the correlation between composition from (WDS) and (ICP) as a function of Raman peak intensity. From both plots a positive correlation of cation disorder peak at 590 cm^{-1} is seen with Ba and Zr unite cell, and excess of dBaCu and the factor dBaCu*(Zr+Hf) as well, which have related to formation of nanorods by addition of doping elements and excess of Ba. Therefore, there is an important correlation for cation disorder that must be studied in more detail.



Figure 48. Correlation coefficient between Raman peak intensity and WDS composition.

In addition, in Figure 48 a certain degree of correlation between some of the peaks and Y, and RE unit cell is seen, and no correlation for Cu; however, in Figure 49 an opposite behavior for this variables is observed. The Raman wavelength as a function of (WDS) and (ICP) unit cell was also investigated, but results showed that only (O_{2+}/O_{3-}) peak 331 cm^{-1} correlates with (Zr+Hf) for both methods. The result is suggesting that when the amount of (Zr+Hf) increases, the (O_{2+}/O_{3-}) Raman band shift to lower frequencies approximately from 336 cm^{-1} to 329 cm^{-1} being the lower frequencies related to superconducting phase (see Appendix C and D). Based on the above analysis, we can conclude that this effort needs further investigation and must be extended for a larger sample pool. This approach may help developing stronger

conclusions to assess if Raman bands can predict superconductor's performance and the potential scenarios where this behavior can be predicted with high degree of reliability.



Figure 49. Correlation coefficient between Raman peak intensity and ICP composition.

4.6. Reel to Reel System Design

In this section a design of a reel-to-reel device to feed long length superconductor tapes for quality control and characterization by means of Raman spectroscopy has been developed. This system has been designed to analyze off-line final product to verify the quality of the tape in a faster way than done with conventional methods where the characterization of the material is carried out in linear scan mode in the center of the tape. In this work, we present a scheme to analyze the tape to cover areas not only along "x" but also along "y" direction. The proposed scanning pattern for the reel-to-reel system is presented in Figure 50, which follows a zig-zag

scheme as a result of the movement on the "x" direction from the right to left and "y" from south to north and vice versa at the same time. This design is based on the scanning patterned develop for the R2R SPHM system [107]. However, the main difference from this design to R2R Raman is the acquisition of data, which is accomplished by moving average, where the average of different subsets is analyzed over a period of time. This average allows to identify a representative trend of the data, reducing the impact of random fluctuations on the data acquired and increasing the scan speed.

For the purpose of integrating the Raman system to the R2R mode one must pay special attention to the scan speed where long acquisition time are impractical and inconvenient for collecting data of long tapes length. The current settings of the Raman system place the scanning acquisition parameters to time of 2 s per spot with a 1.25 mW and 25% of available laser power. This results in a power density of ~1 mW/ μ m2 and limits the samples burnout at ~1 μ m spot size with acceptable SNR (values have been approximated to single digits for practical order of magnitude analysis). However, this acquisition time leads to slow scan speed and high overall scanning time acquisition, which for single scans can be admissible but for reel-to-reel mapping becomes unrealistic. Therefore, if the scan speed needs to be increased, the laser spot must continuously move along the entire area allowing the removal of the laser attenuation which would lead to the use of full power of the system without damaging the sample. For example, if 1 μ m laser spot is moving at a rate of 4 μ m or faster, the power level increases by a factor of four in the current system (full power). This results in reduction of scan time per data point from 2 to 0.5 s.

Another approach that can be applied in order to improve scan speed can be by increasing the laser spot size. However, for this approach, it needs to be considered that increasing the diameter size the laser power must be increase as well to maintain an acceptable SNR. Thus, to keep the same power density without sample burnout and increasing the laser spot diameter, the laser power can be increased following the equation (27). For instance, increasing the spot diameter from 1 μ m to 10 μ m leads to laser power increment from 1 mW to 100 mW holding the same power density.

(27)
$$Power \ density = \frac{Power \ Laser \ Beam}{\pi r^2}$$

In this scenario the scan speed increases by a factor of 100 which enables linear scan rates of 2 mm/s. Following the similar reasoning, increase in spot size to 100 μ m will increase maximum power to 10 W, and enable increase in speed by a factor of 10^4 – which is 20 mm/s. This approach can be carried out by implementing beam expanders where the diameter can be increased to the size the order of millimeters.



Figure 50. Proposed scanning diagram for the reel-to-reel system, the sequence presented followed a zig-zag scheme, where the tape moves on x from right to left, south to north and vice versa, and for control of defocus a Z-stage has been design.

Clearly, to increase the scanning speed, it is necessary to increase laser spot diameter or, alternatively, implement a constant movement of the laser over the area investigated instead of scanning point by point. Now, by increasing the laser spot size for example to 1 mm this results in 12 spots across the 12 mm width and with a scan speed of 0.5 m/s this translates 50 mm/s then this results in about 50 x 12 spots per second. Additionally, the acquisition time is reduced from 2 s from current settings to about less than 2 ms.

Shown in Figure 51 is the reel-to-reel system designed for the current Raman spectrometer where 2G-HTS spool tapes are pretended to be scanned. Considering that the Raman spectrometer is join to the microscope and both are fixed to the same position, the R2R system was design to enable scanning acquisition not only in the "x" direction but also along the "y" direction, which will allow to inspect the entire tape following the scheme previously mention in Figure 50.



Figure 51. Reel-to-reel system Raman design. (a) Front view - the scheme of the tape along the x-axis can be observed. (b) Plan view – view of the design at x-y, with the assembly of the three servo motors and the tensor force equipment.

To move the tape from one side to another a 5kg force have been consider for which a force tensor is introduced in the system. The load torque required to start the movements is calculate by multiplying a force (F) by the rotation radius (r) as given in equation (28), here a T_{max} and T_{min} are contemplated for a radius of the tape spool when full (r_f) and empty (r_e), a safety factor (fs) of 2 was also considered for calculations.

$$T = F * r$$

$$T_{max} = F * r_f * fs = 50N * 0.1143m * 2$$

$$T_{max} = 12 N.m$$

$$T_{min} = F * r_e * fs = 50N * 0.0572m * 2$$

$$T_{min} = 5.72 N.m$$
(28)

The results hold a maximum torque of 12 *N.m* that are required to start the work. Additionally, the power at which the work should be done is calculated using equation (29) assuming a speed of 1m/s, where F is the force and v is the linear velocity, and the angular velocity is 167.09 rpm.

$$P = F * v \tag{29}$$

$$P = 50N * \frac{1m}{s} = 50W$$

Based on these results a servo motor with torque and speed control mode is selected with a maximum torque of 7.7 N.m and maximum speed of 1440 rpm. To bring the torque to the requirements a gearhead 5:1 ratio is used. Besides, for monitoring control an encoder is implemented.

Next, to move the vertical assembly on "y" direction a ball screw system was built considering a vertical weight to be between 100 to 150 kg, a speed of 0.1m/s in an elapse time of 0.2s, resulting in an acceleration of 0.5 m/s^2 . For calculation of required torque, the diameter of the lead screw shaft is considered as well as the range of the weight mentioned before using the equation (28). For a ball screw with a diameter of 0.016m the maximum torque for 150 kg mass is:

$$T_{max} = F_{max} * r_{screw \ lead} = 75N * \frac{0.016}{2}m$$

$$T_{max} = 0.6 N.m$$

The power required and angular speed are 7.5 W and 119.36 rpm, respectively. Additionally, to support the movement and keep the stiffness of the system, four ball bearing carriages and guide rails were implemented (see Figure 52).



Figure 52. Ball screw and guide rails for system motion on y direction.

In Figure 53 the design regarding the Z-stage where the sample will be scanned is presented. This design was modeled with the objective to achieve sufficient tape flatness to avoid defocus issues during scanning of tapes. Therefore, the R2R system for Raman will contain two needle bearings to pinch the tape over a stationary ball bearing in the center of the stage where the measurements will be taken. These two-needle bearings will be spring loaded to produce a pressure over the tape to ensure tape flatness. Additionally, a ball screw system controlled with a step motor was added to the Z-stage to maintain the focus control.



Figure 53. Z-stage design with two needle bearing pinch spring loaded to ensure tape flatness. A ball screw system with a stepper motor is used to control focus on z-direction.

The design of R2R Raman system has been presented and is still under development for the extension of the current project, where programing of electronics and codes are being built. However, here is presented an introduction of the current set-up that is under construction. We expect to have this system built and fully operational in a few months.

CHAPTER 5. CONCLUSIONS

Optimization of operating parameters for Raman spectroscopy scanning mode have been successfully achieved for quality control and characterization of REBCO thin films with high throughput and reliable results. The scanning Raman system has been demonstrated to be able to scan 2D areas of 2G-HTS and provide wealth of information. To our knowledge, this is the first time that Raman scanning mode have been develop for evaluating large areas "x" and "y" simultaneously, which is of crucial importance both for off-line and in-line quality control of REBCO long length tapes and in general for electronic tapes.

The protocols developed in this work allow for high quality data acquisition and processing by implementing algorithms to subtract the background, cosmic ray removal, and peak fitting. This approach permits accurate interpretation of the Raman spectra, and this methodology can be applied for analysis of REBCO tape and a wide range of materials under different equipment settings.

The scans of dropout regions proved that Raman spectroscopy as a 2D mapping/scanning tool is strong for both in-line and off-line characterization of superconductors, offering a myriad of detailed information from each single scan. We highlight that micro-Raman spot diameter used here has been $\approx 2\mu m$ mainly due to the availability of the system. With this set up we have been able to achieve great sample scrutiny even when the step size (100µm) was higher than the laser spot diameter. These two parameters must be equal to provide detailed information of the spatial distribution on samples with heterogeneous morphologies. Therefore, in order to obtain the most detailed information over wider areas, the sampling spot size issue could be solved by using larger microscope objectives or alternatively implementing beam expanders as done in the work of Maroni et al. [108] who achieve a maximum spot diameter of 24 μ m without sacrificing spectral resolution. There are several factors such as the power density and acquisition time that must be considered when high throughput is needed. This is an interesting matter that will be investigated in more detail in future work to optimize the quality control process. By implementing 2D mapping Raman, we have demonstrated the capabilities of the system for detection of defect to ensure REBCO films quality.

The uniaxial and biaxial study by polarized Raman spectroscopy demonstrates its suitability to determine texture on REBCO tapes, where the orientation of c-axis grains as well as a-axis grains can be determined. We also demonstrated that uniaxial texture evaluation can be done by non-polarized Raman with high accuracy. However, the analysis of the biaxial texture by polarized Raman is a complex task due to the sample needs to be rotated about the axis \perp to the film surface to determine the in-plane texture. This method is highly effective for in-plane texture, but no suitable for our current settings. A possible solution if the in-plane texture needs to be analyzed is a fiber optic set up to collect data at four different angles. It is an engineering task that can be considered for a real in-line set up.

The reliability of our big-data analysis for correlation among Raman characteristics and sample in-field performance resides approximately in the 0.6 correlation coefficient, some exceptions

close to 0.8. As a proof of concept this study is promising and increasing the samples number, more accurate conclusions can be drawn. To our knowledge this is the first time that this kind of study is carried out.

5.1. Future work

For future work, there are still some aspects to improve regarding the R2R SRS system that needs to be addressed if higher efficiency of the system is desired especially for larger area evaluation off-line and in-line setup. Currently, the design of the R2R system has been proposed and it is in manufacturing stage where the parameter can be tuned up through the system programing which is the next step on the project. On the other hand, in order to increase scan speed by increasing the size spot diameter beam expanders are going to be implemented as facile route to increase the output beam diameter leading to the speed up of the system data acquisition. Ideally the system will be built to test tapes in the 100 m range or longer using Raman spectroscopy and not only would be used for superconductors tapes but also other types of thin films materials such as semi-conductors.

The correlation study is currently under investigation and would be carried out over the next part of the project. This study would be extended for a larger database and other variables would be considered in more depth such as the relation of (Ba+Zr/Cu).





Figure 54. Raman map of a defective sample. (a) Micrograph of the investigated samples where surface defects are observable. (b), (c) The overlap wavelength map and intensity map normalized to O_{2+}/O_{3-} peak on samples photograph. (d) integrated spectra from selected areas.





Figure 55. Raman map of bend crystals over an area $3x8 \ \mu m$ using a 532 nm laser,100x objective lens, and acquisition time of 1 second. (a) The integrated spectra for 1110 scans acquired in this map. (b) Micrograph of the analyzed material. (c) Intensity map showing the location of bend crystal.


Figure 56. Raman map of straight crystals over an area $4x9 \ \mu m$ using a 532 nm laser,100x objective lens, and acquisition time of 1 second. (a) The integrated spectra for 960 scans acquired in this map. (b) Micrograph of the analyzed material. (c) Intensity map showing the location of bend crystal.

Appendix C



Figure 57. (a) Correlation coefficient between Raman peak Wavelength and ICP unit cell composition. (b) Inset of the wavelength assigned to (O_{2+}/O_{3-}) vs critical current density.

Appendix D



Figure 58. (a) Correlation coefficient between Raman peak Wavelength and WDS unit cell composition. (b) Inset of the wavelength assigned to (O_{2+}/O_{3-}) vs critical current density.

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