

Characterization of Coated Conductors Using Raman Spectroscopy Methods

Victor A. Maroni

Argonne National Laboratory, 9700 South Cass Ave., Argonne, IL 60439 USA

Phone 630-252-4547, Fax 630-972-4547, maroni@anl.gov

Abstract—This paper outlines the type of information gained from the use of Raman micro-spectroscopy methods to examine REBCO coated conductor embodiments. The topics covered include (1) the attributes and limitations of Raman spectroscopy when used as a guidance tool for coated conductor performance enhancement, (2) the features, details, differences, and length scales for which Raman is both suitable and informative, (3) the potential applicability of Raman methods for use as ex-situ and in-situ probes of phase and microstructure development (considering both off-line and on-line implementation), (4) the extent to which Raman methods can be used to characterize the underlying buffer layers and diffusion barriers, and (5) the idiosyncrasies and limitations of Raman methods for the comprehensive interrogation of coated conductors, including considerations pertaining to sampling depth and through-thickness measurements.

I. INTRODUCTION

The performance properties of the REBCO coated conductor are acutely sensitivity to imperfections in REBCO stoichiometry, phase chemistry, and microstructure. To sustain a high critical current, the REBCO film must possess a high degree of contiguous biaxial texture with the **a,b** planes aligned parallel to the substrate surface. The film must also be relatively free of non-superconducting phases (NSPs) and properly oxygen doped to produce orthorhombic REBCO. Furthermore, Raman spectroscopy can be used to interrogate many of the telltale characteristics of the REBCO film that influence its current carrying properties and this interrogation can be performed in ambient air in a nondestructive manner.

The Raman effect makes possible the detection of a specific subset of the modes in the phonon density of states of a crystal lattice [1]. The subset that one detects is determined mainly by the collective site symmetries of the elements that make up the crystal [1,2]. The implications of the Raman spectroscopy of REBCO have been under study for over two decades (see [3,4] and references therein). Features, such as, oxygen stoichiometry of the REBCO phase, REBCO texture quality, the occurrence and approximate magnitude of lattice atom disorder in the REBCO, and the presence of typical NSPs that are not generally observable in a collective manner using other individual characterization tools are readily detected by Raman. Raman has also been used effectively for through-process tracking of phase transformations during precursor conversion to REBCO. The following section presents a capsule summary of the underlying basis for the

Raman scattering effects exhibited by REBCO films, and provides some information about what can be learned from Raman studies of buffer/barrier layer assemblies and from the use of Raman spectroscopy as a process monitoring tool.

II. RAMAN OF REBCO Coated Conductors

REBCO Texture and oxygen stoichiometry: The Raman spectra exhibited by REBCO films on coated conductor templates are profoundly influenced by two key factors—the inherent quasi-epitaxial texture of the REBCO film and the oxygen stoichiometry of the REBCO itself [3,4]. Raman spectra are normally excited by monochromatic, coherent laser radiation. In a typical Raman measurement on an REBCO film using a Raman microprobe, the laser strikes the surface of the film normal to the plane of the substrate and therefore (ideally) parallel to the c-axis of the textured REBCO grains. As explained elsewhere [3], orthorhombic (O) and tetragonal (T) REBCO each possess fifteen Raman active vibrational degrees of freedom (referred to herein after as modes). However, in common practice, only the five modes with eigenvectors parallel to the REBCO c-axis are readily detected. The reason for this is not absolutely clear—the five c-axis modes could be resonantly enhanced or the other ten modes, which are a,b plane modes, could be damped by electronic effects in the a,b plane. Also, the relative intensities of the five c-axis modes in a given spectrum depend on the orientation of the REBCO crystal with respect to the electric vector of the excitation radiation [3,4]. Figure 1 shows how the relative intensities of the five c-axis modes of REBCO vary with respect to both oxygen stoichiometry and orientation of the c-axis with respect to the laser. The characteristics of the spectra in this figure explain much of what one observes during the Raman interrogation of textured REBCO films. For example, (1) the peak frequency of the O4 mode varies over a ca. 30 cm⁻¹ range on going from T (O = 6.0) to O (O = 7.0) REBCO and thus provides an indication of oxygen stoichiometry; (2) the O2+/O3- mode is most intense in Raman microscopy when the direction of propagation of the excitation laser (λ) and the REBCO c-axis are parallel ($\lambda//c$) and least intense for $\lambda//a$ or $\lambda//b$; conversely, the symmetric Raman active O4 mode is most intense for $\lambda//a$ or $\lambda//b$ and least intense for $\lambda//c$, therefore, Raman microscopy of textured REBCO films provides information about the orientation of the REBCO grains with respect to the substrate when λ is perpendicular to the substrate which is normally the case in Raman

microprobe examinations of REBCO films. The basis for the intensity variations with respect to orientation seen in Fig. 1 is discussed in [5].

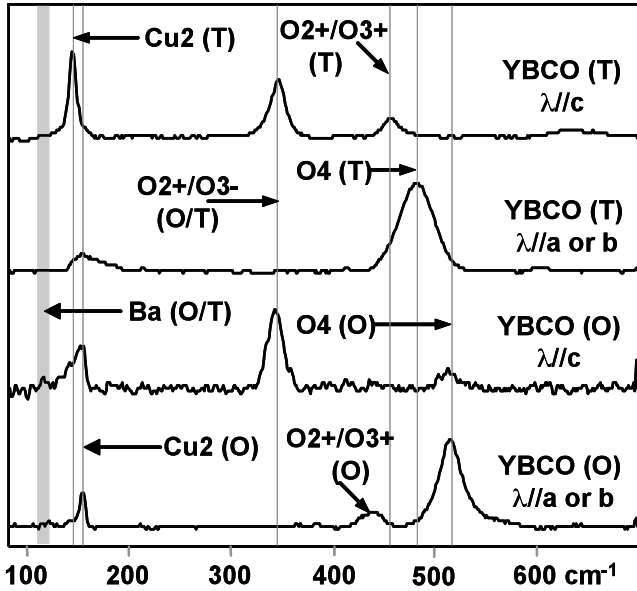


Fig. 1. Typical Raman spectra of orthorhombic and tetragonal REBCO as a function of laser propagation direction (λ) and REBCO crystallographic axis.

Disorder in the REBCO Lattice: Disorder in the cation sub-lattice and/or the oxygen sub-lattice of REBCO is a common occurrence in most REBCO films, particularly those that are produced by ex-situ methods and those that are doped with mixed RE elements or other cations. Disorder in the cation sub-lattice tends to ruin inversion symmetry in such a way that the anti-symmetric infrared active O4 phonon (O4*) appears in the Raman spectrum as a broad band in the 560 to 600 cm^{-1} region [3,6]. In a similar vein, disorder in the oxygen sub-lattice, typically involving the occupation of the O1 site, generates Raman scattering of an inactive Cu1 related phonon at around 230 cm^{-1} [3,4].

Detection of Non-superconducting Second Phases: The most common NSPs found in fully processed orthorhombic REBCO are CuO, BaCuO₂, and Ba₂Cu₃O₅. All three of these phases are readily detected by Raman spectroscopy [3]. CuO has a characteristic phonon near 300 cm^{-1} that often appears as a shoulder on the low frequency side of the O2+/O3- mode of REBCO. The characteristic phonons of the two barium cuprates appear in the 600 to 640 cm^{-1} region. Raman spectra of REBCO films that contain appreciable amounts of RE₂O₃ crystallites often exhibit a shoulder on the high frequency side of the O2+/O3- mode. Raman spectroscopy has been particularly useful for interrogating partially processed metal-organic deposited REBCO films prepared by quenching techniques. Such films normally contain appreciable amounts of RE₂Cu₂O₅, Cu₂O, and RE₂O₃, all of which are easily detected by Raman spectroscopy. However, the characteristic modes of other phases known or presumed to be present during precursor conversion, like BaF₂ and metal oxy-fluorides, have not been detected in the Raman spectra of the quenched samples.

Penetration Depth and Through-thickness Examination: As demonstrated and discussed elsewhere [3], Raman excitation of REBCO films using visible lasers does not produce detectable scattering at depths greater than ca. 200 nm. Therefore, the useful information gained from Raman examination is roughly limited to the topmost 200 REBCO unit cells. In recent years, this limitation has been overcome (and actually turned to advantage) by stepping samples in ca. 200 nm increments [6] or dimpling a tapered slope from the top surface of the REBCO film to the REBCO/substrate interface to allow complete through-thickness examination in ca. 200 nm depth increments [7]. In addition to permitting a full analysis of the REBCO film, it is also possible to interrogate the buffer/barrier films under the REBCO. CeO₂, LaMnO₃, Y₂O₃, and numerous other buffer/barrier materials exhibit characteristic phonons that can be detected by Raman. Also, BaCeO₃, a known reaction product of REBCO and CeO₂, has a characteristic Raman active phonon.

On-line and Off-line Process Monitoring: Very little has been done to explore the utility of Raman-based process and product monitoring tools. A recent paper [8] describes some on-line examinations done on REBCO coated tape exiting a metal-organic chemical vapor deposition (MOCVD) reactor at SuperPower, Inc. The results of this study showed that interpretable length-averaged Raman spectra could be obtained from moving tape, where the averaging length per spectrum was on the order of 1.5 cm.

ACKNOWLEDGMENT

This research was sponsored by the U.S. Department of Energy (DOE), Office of Electricity Delivery and Energy Reliability, as part of a DOE program to develop electric power technology, under contract DE-AC02-06CH11357 between UChicago Argonne, LLC and the DOE.

REFERENCES

- [1] J.C. Decius and R.M. Hexter, *Molecular Vibrations in Crystals*, McGraw-Hill, Inc., 1977.
- [2] W.G. Fateley, N.T. McDevitt, and F.F. Bentley, *Appl. Spectrosc.* 25, pp. 155-173, February 1971.
- [3] K. Venkataraman, R. Baurceanu, and V.A. Maroni, *Appl. Spectrosc.*, 59, pp. 639-649, May 2005.
- [4] M.N. Iliev, in *Spectroscopy of Superconducting Materials*, E. Faulques, Ed., ACS Symposium Series 730, American Chemical Society, pp. 107-119, 1999.
- [5] N. Dieckmann, R. Kursten, M. Lohndorf, and A. Bock, *Physica C*, 245, pp. 212-218, April 1995.
- [6] V.A. Maroni, Y. Li, D.M. Feldmann, and Q.X. Jia, *J. Appl. Phys.*, 102, pp. 113909-1 to 113909-5, December 2007.
- [7] D. Miller, V. Maroni, and V. Selvamanickam, "The Argonne SuperPower CRADA: Characterization of Coated Conductors," 2008 DOE High Temperature Superconductivity Program Peer Review, slides available at: http://www.energetics.com/supercon08/pdfs/presentations/wednesday/2G/6_2g_anl_crada_characterization.pdf.
- [8] V.A. Maroni, J.L. Reeves, and G. Schawb, *Appl. Spectrosc.*, 61, pp. 359-366, April 2007.