Local structural study of commercial grade $MBa_2Cu_3O_{7-x}$ (M = Y and/or Gd) coated conductors by polarized Raman spectroscopy

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Abstract

In 1987, M. K. Wu and Paul Chu discovered $Y_{1.2}Ba_{0.8}CuO_4$ (YBCO) with critical temperature (T_c) of 93 K. It has significantly lowered the cost of cooling of a material up to the point where superconductivity set in. Utilizing the cost reduction of attaining superconductivity and the vast amount of research to understand characteristics of high temperature oxide superconducting materials, there has been effort to use a high temperature superconductor as a coated conductor. It is important to characterize the materials precisely for stable performance before commercializing. We used polarized Raman scattering spectroscopy to study structural and stoichiometric information regarding $YBa_2Cu_3O_{7-x}$, $GdYBa_2Cu_3O_{7-x}$, and $GdBa_2Cu_3O_{7-x}$ produced by three leading groups of producing commercial grade high temperature superconductor coated conductors American Superconductor Corporation, Superpower, and SuNAM.

Keywords: *Commercial-grade Coated Conductors, Polarized Raman spectroscopy, Microstructure*

1. INTRODUCTION

In 1986, J. Georg Bednorz and K. Alex Müller synthesized barium-doped compound of lanthanum and copper oxide with critical temperature of 35 K [1]. It was the first high critical temperature (T_c) superconductor (HTS) found in ceramic materials. After that discovery, many researchers having been tried to find superconductors with higher T_c, and now HTS of mercury barium calcium copper oxide ($HgBa_2Ca_2Cu_3O_8$) with critical temperature as high as 133 K have been synthesized [2, 3]. The first superconductor which has higher T_c than the boiling point of liquid nitrogen (77 K) is $YBa_2Cu_3O_{7-x}$. In this compound, T_c is maximized near 93 K around x = 0.15 with the orthorhombic structure. However, superconductivity disappears in $YBa_2Cu_3O_{7-x}$ around x = 0.6 with tetragonal structure [4]. From 2000s, studies of rare earth materials such as gadolinium (Gd), samarium (Sm) replacing yttrium (Y) have been performed in many research groups and companies.

Coated conductors (CCs) have good characteristics for using in application to cables, generators and transformers [5, 6]. Recently, companies have been developing optimized methods to make coated conductors using HTS [7]. Among them, American Superconductor Corporation (AMSC), Superpower and SuNAM are leading the development of coated conductors. CCs are fabricated with metal organic chemical vapor deposition [8, 9], metal-organic deposition [10, 11] and/or co-evaporation [12, 13] in these companies. But each of CCs shows different characteristics such as performance, cost, and production rates because of the materials in superconducting layer and buffer layers are all different company by company.

In this study, we studied local structural properties by polarized micro-Raman measurement about three commercial-grade CCs produced by AMSC, Superpower, SuNAM. In addition to the structural information that can be obtained, e.g., by XRD, polarized micro-Raman scattering measurements can provide information such as distribution of second phase in the surface and the orientation of grains in micrometer scale.

2. EXPERIMENTS

Three sets of coated conductor samples were prepared for this study: The first sample is $YBa_2Cu_3O_{7-x}$ (YBCO) made by AMSC. This sample was fabricated by metal organic deposition (MOD) and the structure of this sample is Ag (1 μm) / YBCO (1 μm) /CeO_2 (75 nm) / YSZ (75 nm) / Y_2O_3 (75 nm) / metal alloy substrate (50 – 75 μm). Buffer layers are fabricated by solution-based processing [14]. The second one is $(Gd,Y)Ba_2Cu_3O_{7-x}$ (GdYBCO) made by superpower. This sample was fabricated by metal organic chemical vapor deposition (MOCVD) and the structure of this sample is Cu stabilizer (20 μm) / Ag (2 μm) / GdYBCO (1 μm) / buffer stack (1 μm) / substrate (50 μm) [15]. The third one is $GdBa_2Cu_3O_{7-x}$ (GdBCO) made by SuNAM. This sample was fabricated by reactive co-evaporation by deposition and reaction (RCE-DR) and the structure of this sample is Ag (1 μm) / GdBCO (1.5 μm) / $LaMnO_3$ (20 nm) / MgO (60 nm) / Y_2O_3 (7 nm) /Al_2O_3 (50 nm) / Hastelloy [16]. The details of the fabrication method of each sample are shown in [17-19].

To measure the three sets of samples, polarized

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Micro-Raman measurements were performed. Samples were excited with 10 mW of 488 nm (2.54 eV) diode laser focused to 1 μm diameter spots using 100x microscope objective. For polarization measurement, the spectra were obtained with the incident and scattered light polarized in the following configurations in order to identify the symmetries of the phonon modes studied: $(E_i, E_s) = (X, X)$, $(E_i, E_s) = (X', X')$, $(E_i, E_s) = (X, Y)$, $(E_i, E_s) = (X', Y')$, where E_i and E_s are the incident and scattered electric-field polarizations, respectively, X, Y, X', Y' are the [100], [010], [110], and [1$\bar{1}$0] crystal directions, respectively. In our polarized Raman measurements, the angle between the polarization of the incident light and a nanowire was changed by rotating the incident polarization. When the polarization of the scattered light is parallel (perpendicular) to that of the incident light, we name that configuration parallel (perpendicular) polarized Raman measurement.

3. RESULT AND DISCUSSION

The crystal structure of MBa$_2$Cu$_3$O$_7$ (MBCO) is shown in Fig. 1. In this figure, only the middle atom in the unit cell, denoted by M, is different between YBCO (M=Y) and GdBCO (M=Gd). These materials can have either orthorhombic or tetragonal phase, and superconducting properties are only observed in orthorhombic phase. The SEM images of each coated conductor are shown in Fig. 2. YBCO (a) has small grain size compare to GdYBCO (b) and GdBCO (c). As shown in Fig. 2, GdYBCO and GdBCO have some irregular pattern and this pattern shows different color in optical microscope (Figs. 4 (c) to (f)).

Unpolarized Raman spectra are shown in Fig. 3. In this figure, there are 5 peaks (140 cm^{-1}, 210 cm^{-1}, 333 cm^{-1}, 448 cm^{-1}, 494 cm^{-1}) seen in YBCO, there are 6 peaks (143 cm^{-1}, 294 cm^{-1}, 335 cm^{-1}, 400 cm^{-1}, 500 cm^{-1}, 630 cm^{-1}) observed in GdYBCO and the spectrum of GdBCO shows 6 peaks (143 cm^{-1}, 295 cm^{-1}, 326 cm^{-1}, 344 cm^{-1}, 502 cm^{-1}, 631 cm^{-1}). It is well-known that 140 cm^{-1} (YBCO) and 143 cm^{-1} (GdYBCO) peaks are A$_g$ mode induced by Cu-Cu stretching motion, 210 cm^{-1} of YBCO is related to the oxygen disorder at the Cu(1)-O(4)- chains and 448 cm^{-1} of
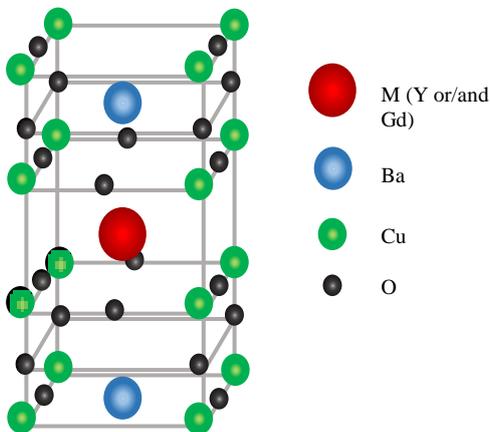
YBCO and 400 cm^{-1} of GdYBCO are mainly due to in-phase z-displacements of the O(2) and O(3) oxygen atoms (A$_g$ mode), respectively [20]. 294 cm^{-1} of GdYBCO and 295 cm^{-1} of GdBCO came from second phase of CuO [21]. Main peaks that are not related to either disorder or second phases of MBCO (M = Y and/or Gd) exist around 330 cm^{-1} and 500 cm^{-1}. 333 cm^{-1} of YBCO, 335 cm^{-1} of GdYBCO and 326 cm^{-1} of GdBCO are associated with the same out-of-phase Ag mode in the CuO$_2$ plane (O(2)+/O(3)) [22].
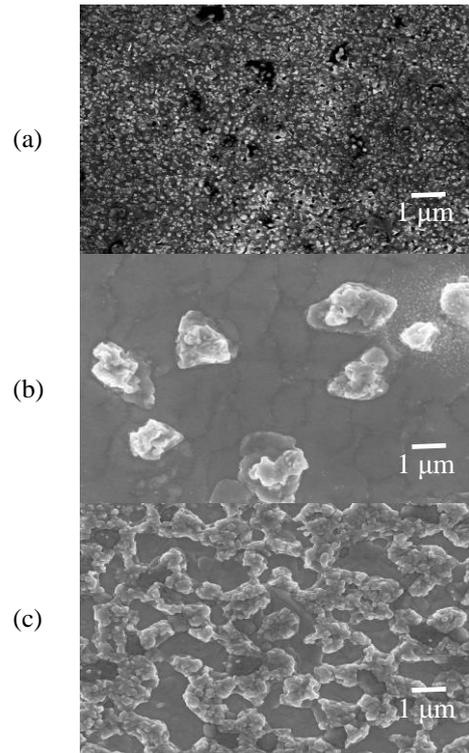

Fig. 2 .SEM images of YBCO (a) , GdYBCO (b) and GdBCO (c).
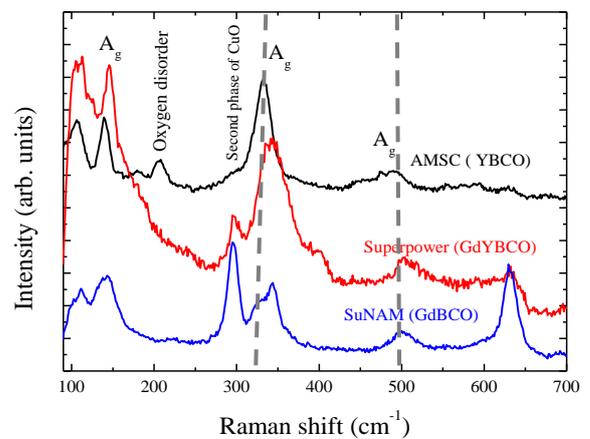

Fig. 3. Unpolarized Raman spectra of each CC. The spectra are offset for clarity. Dashed lines denote the frequencies of the O(2)+/O(3) mode (around 330 cm^{-1}) and the apical oxygen (A$_g$) mode (around 500 cm^{-1}).

Fig. 1. Crystal structure of orthorhombic phase MBCO.

In the case of pure orthorhombic structure the O(2)+/O(3) mode should have A_g symmetry, but in the oxygen undepleted YBCO, the mode behaves like a B_{1g} mode [20]. Because a phonon mode frequency depends on the mass of the vibrating atom, difference in atomic mass of Y (88.906 g/cc) and Gd (157.25 g/cc) is to be seen as the relative peak positions in Raman spectra. In Raman measurements, a peak of GdBCO has lower frequency than that of YBCO because Gd is heavier than Y. 494 cm^{-1} of YBCO, 500 cm^{-1} of GdYBCO, 502 cm^{-1} of GdBCO are A_g modes due to apical O(4). This mode is related to the oxygen contents and the vibration is along the *c*-axis. This mode tends to shift toward lower frequency when oxygen is insufficient and also largely reflects the structural disorder. From these two main modes, we can figure out the structural orientation of the samples. These samples can be grown into either the *a*-axis or the *c*-axis orientation. According to the Raman selection rule the *a*-axis oriented grains should not show O(2)+/O(3) peak [23]. However, we clearly observed the O(2)+/ O(3) mode in all of the three samples so it is apparant that our samples have *c*-axis orientation.

From the optical images in Fig. 4 (c) to Fig. 4 (f), GdYBCO (c), (d) has many different colored grain (black, white, orange) and grain sizes are bigger than other samples. In this sample, overall Raman spectra in range of 100 cm^{-1}

to 700 cm^{-1} was similar but higher frequency after 700 cm^{-1} shows dependence on the grain the data are taken. Some black colored grain has intense oxygen peak in 240 cm^{-1} and 500 cm^{-1} to 630 cm^{-1} (Fig. 4 (a)). Also more of second phase of CuO in 294 cm^{-1} are observed in the black part . GdBCO (d), (f) has many different colored grains but size of the grains is much smaller than that of GdYBCO. Raman spectra of GdBCO is rather homogeneous with respect to the position but some white spot does not show the apical O(4) mode and O(2)+/O(3) mode (Fig. 4 (b)). From these result, we can conclude that the black part contain more oxygen and in the case of GdYBCO, it contains more second phase of CuO than the white part.

Polarized Raman measurement can provide information regarding the structure of a sample. $MBa_2Cu_3O_{7-x}$ is P_{mmm} space group and it can be grown either into orthorhombic or tetragonal structure and we can calculate the Raman activity of particular vibration modes that depends on the polarization configuration by using Raman tensor (Table 1 (a)). There are four Raman active A_g, B_{1g}, B_{2g}, and B_{3g} modes in the orthorhombic structure, and five modes of A_{1g}, A_{2g}, B_{1g}, B_{2g}, and E_g are Raman active mode in the tetragonal structure of MBCO. Raman tensors of these modes are shown below [24].
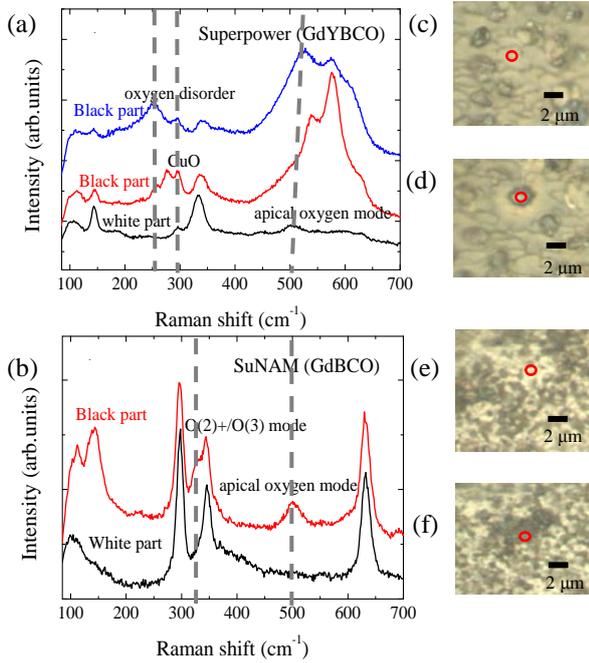

Fig. 4. Unpolarized Raman spectra of GdYBCO (a) and GdBCO (b) taken at different locations on the sample. Dashed lines in (a) represent the oxygen disorder (240 cm^{-1}), the second phase of CuO (294 cm^{-1}), and the apical oxygen (A_g) mode (around 500 cm^{-1}) frequencies. Dashed lines in (b) is the O(2)+/O(3) mode (around 330 cm^{-1}) and the apical oxygen (A_g) mode (around 500 cm^{-1}). (c) and (e) are white part of the sample (denoted by a red circle) and (d) and (f) are black part of the sample (denoted by a red circle).

TABLE 1
RAMAN ACTIVE MODE OF EACH POLARIZATION CALCULATED BY RAMAN TENSOR OF SPACE GROUP P$_{mmm}$ (A). IDENTIFYING THE STRUCTURE OF YBCO (B), GDYBCO (C) AND GDBCO (D) BY RELATIVE INTENSITY OF EACH POLARIZATION. S IS STRONG INTENSITY, W IS WEAK INTENSITY

orthorhombic		Tetragonal	
XX	A_g	XX	A_{1g},B_{1g}
XY	B_{1g}	XY	B_{2g}
X'X'		X'X'	A_{1g},B_{2g}
X'Y'	A_g,B_{1g}	X'Y'	B_{1g}

YBCO Peak position(cm^{-1})					
Peak	210	140	333	448	494
XX	S	S	S	W	W
XY	S	W	W		
X'X'	S	S	W	W	W
X'Y'	W	W	S		
Ortho		A_g	A_g	A_g	A_g
Tetra	A_{1g},B_{2g}	A_{1g}	B_{1g}	A_{1g}	A_{1g}

GdYBCO Peakposition(cm^{-1})					
Peak	143	294	335	500	630
XX	S	W	S	W	
XY	W	W	W	W	W
X'X'	S	W	W	W	W
X'Y'	W			W	W
Ortho	A_g		A_g	A_g	B_{1g}
Tetra	A_{1g}	A_{1g},B_{2g}	A_{1g},B_{1g}	A_{1g}	B_{2g}

GdBCO Peakposition(cm^{-1})						
Peak	143	295	326	344	502	631
XX	S	S	S	S	S	W
XY	S	W	W	S	W	S
X'X'	S	S	W	W	W	W
X'Y'	W	W	S	W	W	W
Ortho		A_g	A_g	A_g,B_{1g}	A_g	B_{1g}
Tetra	A_{1g}	B_{1g}			A_{1g}	B_{2g}

$$A_g = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix} \quad B_{1g} = \begin{pmatrix} 0 & d & 0 \\ e & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$B_{2g} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & f \\ 0 & g & 0 \end{pmatrix} \quad B_{3g} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & h \\ 0 & i & 0 \end{pmatrix}$$

These are Raman tensor in the orthorhombic structure. We can calculate the Raman activity in a particular polarization configuration by multiplying the polarization state of light into the Raman tensors. Then, we can figure out the A$_g$ mode is to be observed in XX, X'X' and X'Y' polarization configurations and the B$_{1g}$ mode is to be seen in X'X' and X'Y' polarization configurations. B$_{2g}$ and B$_{3g}$ modes cannot be observed in the *c*-axis orientation.

$$A_{1g} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix} \quad A_{2g} = \begin{pmatrix} 0 & c & 0 \\ -c & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$B_{1g} = \begin{pmatrix} d & 0 & 0 \\ 0 & -d & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad B_{2g} = \begin{pmatrix} 0 & e & 0 \\ e & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$E_g = \begin{pmatrix} 0 & 0 & f \\ 0 & 0 & 0 \\ g & 0 & 0 \end{pmatrix} \quad \text{or} \quad \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & f \\ 0 & g & 0 \end{pmatrix}$$

These are Raman tensor in the tetragonal structure. By following the same procedure as with the orthorhombic structure, we can figure out the A$_{1g}$ mode is to be observed in XX and X'X' polarization configuration, the B$_{1g}$ mode is to be observed in XX and X'Y' polarization configuration, and the B$_{2g}$ mode is to be seen in XY and X'X' polarization configuration. A$_{2g}$ and E$_g$ modes cannot be observed in the *c*-axis orientation. From these result, we could confirm that this samples are c-axis oriented

Fig. 5 plot polarized Raman spectra of the three samples. Table 1 shows the relative peak intensity of the three samples. From relative peak intensity of four polarization configurations, we can assign the Raman modes of each possible structure. In reference, all Raman modes of YBCO are A$_g$ mode, especially O(2)+/O(3) mode and apical O(4) modes are A$_g$ mode. According to our result of the polarization depenence of A$_g$ modes, it is confirmed that the three samples have orthorhombic structure.

Fig. 5. Polarized Raman spectra of YBCO (a), GdYBCO (b) and GdBCO (c). X' and Y' are 45° tilted polarizations of X and Y polarization, respectively. Dashed lines are main peak of MBCO (A$_g$ mode of 330 cm^{-1} and 500 cm^{-1}).

with respect to the polarization configuration by using Raman tensor and comparing to parallel (XX and X'X') and two cross (XY and X'Y') polarization Raman measurements confirm that the three samples we studied have orthorhombic structure. Our results suggest that polarized Raman scattering spectroscopy can be effectively used as a local probe that can provide information regarding orientation and crystalline structure as well as the distribution of the secondary phase in micrometer scale.

4. CONCLUSION

To study the local structure of MBCO coated conductor, we used polarized Raman spectroscopy. As contents change from Y to Gd, the O(2)+/O(3) mode near 330 cm^{-1} red shifts. The apical O(4) mode near 500 cm^{-1} exhibits higher intensity in the black part of the optical image, which suggests that the black part contains more oxygen. Existence of the O(2)+/O(3) mode can show that these samples are *c*-axis oriented. Calculating Raman activity of the A$_g$ mode of O(2)+/O(3) mode and apical O(4) modes
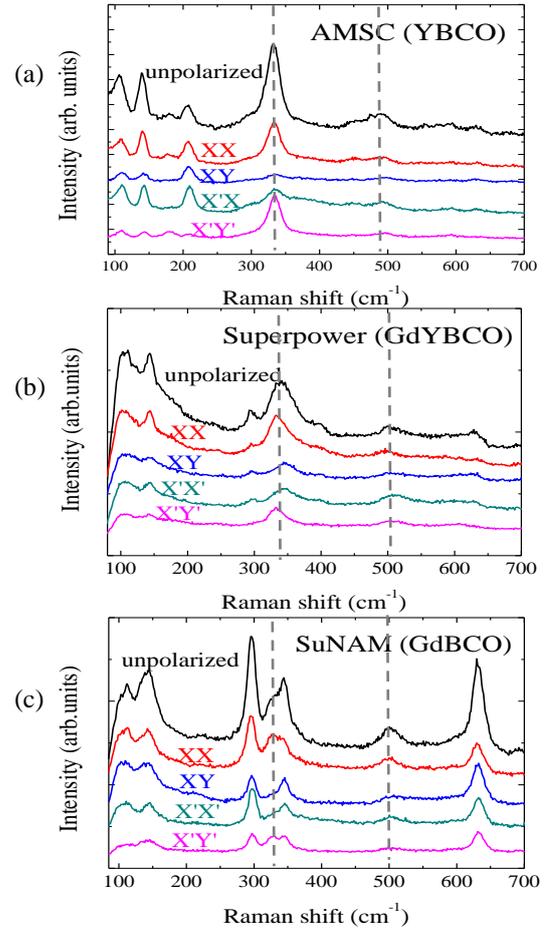
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