Comparison of the Effect of Graphene and Graphene Oxide Doping on YBCO

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Abstract. Weak-links in high temperature superconductors (HTS) are a result of an incorrect stoichiometric ratio found in grain boundaries and misaligned planes. These weak-links severely decrease the critical transport current of the bulk HTS material (such as YBCO) and increase resistance in the normal state. Bulk YBCO was doped with graphene oxide (GO) and reduced graphene oxide (rGO) in the following dopant concentrations: 0, 0.1, 0.5, 0.7, 0.9 and 1 % wt. Through mechanical hardness testing, it was observed that the hardness of the samples increased as the GO and rGO concentration increased. The 1 % wt. doped GO and rGO samples was observed to be hardest, with a true hardness of 2.630 GPa and 2.405 GPa respectively, compared to the control sample with a true hardness of 1.499 GPa. Critical transition temperature ($T_c$) of the GO doped YBCO samples are greater than rGO doped samples and is presumably related to the higher oxygen content found in GO. The 0.7 % wt. doping for GO and rGO samples had the highest critical transition temperature of 98 K and 91 K, respectively. Both GO and rGO samples showed a decrease in normal resistance up to 0.7 % wt. doping, compared to the control sample. The weak-link effect was most improved in the 0.7 % wt. doped samples for GO and rGO.

1. Introduction

YBCO was discovered in 1987 with a critical transition temperature of 92 K [1]. This was of importance as 92 K is above the boiling point of liquid nitrogen. There has been constant research in order to improve mechanical and superconducting properties of bulk YBCO material. Poor critical current of bulk YBCO material is attributed to a network of weak-links in bulk material [2]. Magnetic levitation applications, such as flywheels, are also hindered due to the fact that the repulsive force between the permanent magnet and the superconductor will be weak. This is caused by the superconductor being unable to generate large surface currents to produce an opposite and equal magnetic field to allow for magnetic levitation in stronger fields [3].

In levitation applications, an increase in flux pinning sites can help improve magnetic stiffness, thus increasing stability in the lateral axis of levitation [4]. This increase in magnetic stiffness allows for improved damping and a larger region of stability [5]. This improvement in the stability allows for larger angular velocities, thus increasing the amount of energy stored [4] [6].
Past research has shown that doping bulk YBCO material can improve its mechanical and superconducting properties. Doping YBCO with silver decreases its normal resistivity, increases flux pinning sites and its critical current density [2]. Zinc Oxide doping of YBCO improves hardness of the material [7]. Graphene oxide doping of MgB$_2$ has been reported to improve the grain boundary connectivity, increase critical current and the number of flux pinning sites [8]. Graphene oxide (GO) doping of YBCO has been found to improve flux pinning, grain connectivity, increase $T_C$ and critical current in bulk material [9].

There has been a number of studies on the doping of YBCO with GO [9] [10], but no comparison of GO and reduced GO (rGO). In this research, YBCO bulk material was doped with GO and rGO in order to study the role that oxygen and graphene play in observed improvements in bulk material.

2. Experimental

GO was produced using the Hummers method with additional potassium permanganate [11]. GO was reduced to rGO using NaBH$_4$ and CaCl$_2$ as a catalyst [12]. YBCO bulk powder obtained from Superconductor Technologies Inc. was doped with GO and rGO in the following concentrations: 0, 0.1, 0.5, 0.7, 0.9, and 1 % wt. Thereafter, these powders were pressed into pellets with a diameter of 12 mm and a thickness of 2 mm at pressure of 45 MPa. Pellets were then sintered at 950˚C in an oxygen atmosphere for 6 hours. $R$ vs. $T$ measurements were taken in field cooled (FC) and zero field cooled (ZFC) conditions. Resistance was measured using the four wire resistance method. In order to measure the foot structure of the $R$ vs. $T$ curves to determine the effect on the weak-links, a variable of $\Delta T_C$ was defined as:

$$
\Delta T_C = T_{\text{ONSET}} - T_{\text{OFF}},
$$

where $T_{\text{ONSET}}$ is the temperature at which the transition from the normal to the superconducting state begins and $T_{\text{OFF}}$ is the temperature at which the superconducting state is reached.

Vickers hardness testing was carried out at a temperature of 297 K. The following load forces were applied: 25 g, 50 g, 100 g, 200 g and 300 g with a load contact time of 10 s using a pyramid indenter shown in figure 1. Several indentations were made for each load in order to achieve the optimum mean value for Vickers hardness, $H_v$.

Equation 2 was used to determine $H_v$, were $d$ is the mean value of diagonals $d_1$ and $d_2$ measured from the indentation on the sample surface seen in figure 2 and $F$ is the applied load [7].

![Figure 1. Vickers hardness indenter applying load on sample surface.](image1)

![Figure 2. Diamond shaped indentation on sample surface.](image2)
There are two types of models to describe load dependent hardness [13]. One model considers energy-dissipative processes and the other model considers elastic processes during indentation. The energy-dissipative processes approach was considered [13]. In order to determine a true load independent hardness, $H_0$, the following equation was used,

$$H_0 = 1854.4 \frac{F - F_O}{d^2}$$  \hspace{1cm} (3)

where $F_O$ is the energy dissipative portion of the load [7] [13]. $H_0$ and $F_O$ were determined from the plot of $F$ vs. $d^2$.

3. Results and discussion
Figure 3 (a) and figure 3 (b) shows transmission electron microscope (TEM) images of 2D sheet structure of GO and rGO, respectively. A fold can be seen in the GO sheet in figure 3 (a) and the rGO sheet in figure 3 (b) is crumpled.

Fourier transform infrared spectroscopy (FTIR) in figure 4 was used to determine the amount of oxygen groups in the graphite, GO and the rGO material. The O-H group in the graphite sample is due to intercalated water which occurs in natural graphite, the precursor material used for the production of GO [14]. Oxidation of the graphite to produce GO can be seen by the increase in oxygen functional groups and the increase in the size of the O-H peak in the GO sample. In the rGO sample, the oxygen functional groups are reduced which can be seen by the reduction in peak sizes compared to the rGO sample. This can be seen by the reduction in the size of the O-H, C=O and C-O peaks.
Figure 4. FTIR for graphite, GO and rGO.

The RAMAN spectrum of GO and rGO are shown in figure 5 and are consistent with typical RAMAN spectrum plots to be found in other studies of GO and rGO [15] [16]. The D band is a result of out of plane vibrations which is due to structural defects and the G band is caused by in plane vibrations of sp$^2$ carbon atoms [15]. The D peaks occur at 1363 cm$^{-1}$ and 1348 cm$^{-1}$ and G peaks at 1589 cm$^{-1}$ and 1579 cm$^{-1}$, in GO and rGO respectively. The intensity of the D peak is greater in GO than in rGO which is due to a larger number of defects in GO. This results in the disruption of sp$^2$ bonds thus creating more sp$^3$ bonds [15] [16]. The G peak in rGO is shifted to a lower wave number compared to GO which is due to an increase in the number of sp$^2$ bonds [16].

The full width half maximum (FWHM) of the D peaks for GO and rGO are 177.76 and 54.45 and for the G peaks it is 101.69 and 50.02 respectively. The decrease in the FWHM for the D and G bands from the GO to reduction to rGO signifies a decrease in disorder in the rGO material which is associated with a reduction in oxygen [15] (this reduction of oxygen in the form of bubbles was observed during the reduction step of GO to rGO when the NaBH$_4$ was added to the GO solution) [15]. The 2D band in the rGO occurs at 2644.08 cm$^{-1}$ and is a unique feature of GO approaching true graphene (G) material. The ratio of $I_{2D}$ / $I_G$ for the rGO is 0.32 which means that it is multi layered [17].

Figure 5. RAMAN spectrum of GO and rGO

The transition from superconducting to a complete normal state occurs over a smaller temperature range in rGO doped samples than in GO doped samples, as shown in figure 6 and figure 7. In Table 1, $\Delta T_C$ characterizes this transition and is seen to be smaller in rGO doped samples compared to GO doped...
samples. This decrease in foot structure in rGO doped samples compared to GO doped samples signifies a reduction in weak-links at the grain boundaries in rGO samples than in GO doped samples [18].

The critical transition temperature $T_{\text{Cmid}}$ is defined as the mid-point between the $T_{\text{Cons}}$ and the $T_{\text{Coff}}$ [19]. This is shown for GO and rGO samples in Table 1 and are all greater than the control. The transition temperature for GO doped samples are greater than rGO doped samples. This is due to the GO having a higher oxygen content than rGO, resulting in better oxygenation of the grains in GO doped samples than rGO doped samples [9] [10].

**Table 1. Analysis of ZFC curves.**

| Sample                  | Control | GO doped YBCO (% wt.) | rGO doped YBCO (% wt.) |
|-------------------------|---------|-----------------------|------------------------|
|                         | 0.1     | 0.5       | 0.7       | 0.9       | 1        | 0.1     | 0.5       | 0.7       | 0.9       | 1        |
| $T_{\text{Cmid}}$ (K)   | 84      | 90        | 92        | 98        | 93       | 91      | 86        | 88        | 91        | 89       | 85     |
| $\Delta T_C$ (K)        | 13      | 13        | 11        | 8         | 12       | 10      | 8         | 7         | 4         | 5        | 6     |
| Resistance at $T = 120$ K (Ω) | 0.225   | 0.181     | 0.136     | 0.099     | 0.161    | 0.182   | 0.163     | 0.163     | 0.138     | 0.187    | 0.220 |

The normal resistivity of GO and rGO doped samples shown in Table 1 are smaller in comparison to the control sample. This could be attributed to GO and rGO being reduced to nearly pure graphene during the sintering process at temperatures above 650°C, that is, thermal reduction. Graphene, being a good conductor, would improve grain boundary connectivity in samples thereby reducing the normal resistance [9].

**Figure 8. Applied Magnetic Flux density vs. $\Delta T_C$ for GO doped samples.**

**Figure 9. Applied Magnetic Flux density vs. $\Delta T_C$ for rGO doped samples.**
FC measurements of the samples are shown in figure 8 and figure 9. It can be seen that $\Delta T_C$ of the samples increase with an increase in the applied magnetic field. This is a manifestation of the grain-boundary weak-link effect. $\Delta T_C$ of GO and rGO samples are smaller than that of the control sample thus showing an improvement in grain boundary connectivity. rGO doped samples have a lower $\Delta T_C$ than GO doped samples for the same dopant weighting. Generally, the 0.7 % wt. doped sample for GO and rGO sample sets exhibit the most improved grain connectivity.

The load dependent hardness relationship is shown in figure 10. It is observed that as the applied load force increases, the $H_v$ decreases for all samples and reaches a plateau. This is referred to as the indentation size effect (ISE). This ISE behavior is attributed to grain boundaries and impurity phases in the material [20]. The improvement in hardness in the doped samples, as shown in figure 10, can be attributed to improved locking of grain boundaries due to solute solution strengthening. Solute solution strengthening occurs when the dopant, in this case GO and rGO nanocarbon structures, create localized strain fields. This locks defects in the material, inhibiting their motion and increasing the material’s hardness [21].

Table 2 shows the true load independent hardness, $H_0$, and the energy dissipative portion of the load, $F_D$, which calculated using the graphs ($F$ vs. $d^2$) was shown in figure 11. $F_D$ increases with an increase in doping concentrations of GO and rGO. The true hardness values of the sample increase with the increase in GO and rGO doping. The hardness of 0.1 % wt. doped GO and rGO samples are approximately equal. As the doping concentration increases, the hardness of the GO doped samples are greater than the rGO doped samples.

| Sample | Control | 0.1 % wt. | 0.5 % wt. | 1 % wt. |
|--------|---------|-----------|-----------|---------|
|        |         | GO        | rGO       | GO      | rGO     | GO      | rGO     |
| $H_0$ (GPa) | 1.499 | 1.703 | 1.721 | 2.264 | 2.197 | 2.630 | 2.405 |
| $F_D$ (N)  | 0.021 | 0.067 | 0.021 | 0.013 | 0.087 | 0.137 | 0.161 |

Figure 10. Vickers hardness, $H_v$, vs. applied load, $F$, for GO and rGO doped samples.

Figure 11. Applied load, $F$, vs. the diagonal of the impression squared, $d^2$, for GO and rGO doped samples.
The greater increase in the hardness of GO doped samples compared to rGO doped samples can be attributed to the GO dopant creating a larger amount of strain in the sample than the rGO dopant. This is due to the fact that rGO has a greater thermal stability compared to GO [22] [23]. Heating up GO to temperatures above 650°C during the sintering process results in the oxygen functional groups being removed, creating thermally reduced GO (T-rGO) [9]. This has a greater surface area than chemically reduced GO (C-rGO) [24]. This increase in surface area of dopant inside the sample results in an increase in strain, thus allowing for better locking of defects [7] [21].

4. Conclusion

The results show that doping of bulk YBCO with GO and rGO increases the samples \( T_c \) up until 0.7 % wt. for both dopants. The increase in \( T_c \) for GO doped samples are greater than in rGO doped samples. This shows a direct correlation to the influence of oxygen on the \( T_c \) of YBCO from GO doping. There is also a notable decrease in the normal resistance with both dopants up to 0.7 % wt.

In GO and rGO doped samples, the weak-link effect has been significantly improved which is attributed to better pinning in the grain boundaries. The weak-link effect in rGO samples has improved more than in GO samples, possibly due to an increase in pinning sites as rGO will contain more nanocarbon than GO for the same weight.

Vickers hardness of both GO and rGO samples have increased with an increase in GO and rGO dopants. This is due to solute solution strengthening. The GO doped samples were harder than the rGO samples, with the hardest sample being the 1 % wt. GO doped sample.

The improvement in weak-links at grain boundaries and the increase in flux pinning sites, which is seen by the decrease in foot structure of the GO and the rGO doped samples, will allow for better performance in high current and magnetic levitation bulk applications.

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