Effect of addition of BaTiO$_3$ nano particles on the electrical transport properties of YBCO superconductor

P P Rejith, S Vidya and J K Thomas*

Electronic Materials Research Laboratory, Department of Physics, Mar Ivanios College, Thiruvananthapuram- 695 015, Kerala, India

*e-mail: jkthomasemrl@yahoo.com

Abstract. The flux pinning properties of YBCO bulk superconductors synthesized by conventional solid state route and are added with different weight% ($x=0, 0.5, 1, 2, 3, 5$) of nano BaTiO$_3$ which are prepared by a modified combustion route are studied systematically. The phase analysis of the samples was done by using X-ray diffraction and scanning electron microscopy. Temperature-resistivity measurements, magnetic field dependence of critical current density ($J_c$-B Characteristics) and flux pinning force calculations were done at 77 K. From the SEM images the microstructure of the sample showed a relative uniform distribution of the nano-particles within the specimen. We found that, even though the transition temperature ($T_c$) does not change considerably with the BaTiO$_3$ addition, both the critical current density ($J_c$) and flux pinning force ($F_p$) increased systematically up to 2 wt% BaTiO$_3$ in the composite, in the presence of magnetic field ranging between 0 and 0.6 T. The $J_c$ value in 2 wt% BaTiO$_3$ added sample showed at least 250% larger than that of the pure YBCO. Also the flux pinning force calculated for the 2 wt% BaTiO$_3$ added is found to be enhanced more than 9 times that of pure YBCO. These observations suggest that the BaTiO$_3$ addition to the Y-123 compounds improve the electrical connection between superconducting grains to result in the increase in $J_c$.

1. Introduction

YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) is one of the most widely studied high temperature superconductor, because of its promising and attractive aspects of applications, which include energy storage systems, current limiters, magnetic bearings etc. Improvement of critical current of YBCO materials is attained by the creation of additional defects acting as pinning centers by irradiation, incorporation of nanoparticles and doping [1-3]. Flux pinning by non-superconducting inclusions and crystal defects are also widely studied for YBCO. The main effects of these methods were the inclusion of artificial pinning centers and the introduction of secondary phases related to the additives which results in the enhancement of $J_c$. Here we report the results of our studies on the variation in the electrical transport properties such as $T_c$, $J_c$, and flux pinning force and also the microstructure analysis of YBCO added with different wt% of nanoparticles of BaTiO$_3$ prepared using an auto igniting combustion technique.

2. Experimental

The YBa$_2$Cu$_3$O$_{7-\delta}$ superconductor was prepared through conventional solid state route by thoroughly mixing high purity Y$_2$O$_3$, BaCO$_3$, and CuO in the stoichiometric ratio. The mixture was calcined at 930°C for a total of 72 hours with two intermediate wet grindings. The nano particles of BaTiO$_3$ were
prepared through an auto igniting combustion process. For the typical synthesis, aqueous solution containing ions of Ba and Ti was prepared by dissolving high purity Ba(NO$_3$)$_2$ in distilled water and C$_{12}$H$_{28}$O$_4$Ti in ethanol. Citric acid was then added as the complexing agent. Amount of citric acid was calculated based on total valence of the oxidizing and the reducing agents for maximum release of energy during combustion [4]. Oxidant/fuel ratio of the system was adjusted by adding nitric acid and ammonium hydroxide. The solution containing the precursor mixture at a pH of ~7.0 was heated using a hot plate at ~250°C, which ignites giving nano powder of phase pure BaTiO$_3$. Different wt% of 15nm sized BaTiO$_3$ thus obtained is then added to YBCO, mixed thoroughly, pelletized and sintered at 980±5°C for 24 hours with a heating rate of 3°C/minute. Then the samples was then cooled to 550°C in 8 hours and kept 24 hours for oxygenation.

The structural characterization of YBa$_2$Cu$_3$O$_{7-\delta}$ (Y0), nano crystalline BaTiO$_3$ added YBa$_2$Cu$_3$O$_{7-\delta}$ samples were examined by powder X-ray diffraction (XRD) technique using a Bruker D-8 X-ray Diffractometer. The surface morphology of the sintered samples was studied using Scanning Electron Microscopy (SEM) (JEOL JSM 6390 LV). The critical transition temperature ($T_c$) of both pure and BaTiO$_3$ added samples were measured using standard four probe technique using Keithley source meter 2440 and nano voltmeter 2182A along with lakeshore temperature controller equipped with PT111 platinum sensor. The in-field transport critical current ($J_c$-$B$) measurements were done using a magnetic field set up fabricated indigenously using bipolar electromagnets with required value of current which can generate a maximum field upto 1 Tesla at liquid nitrogen temperature using the four probe method with the standard 1μV/cm criterion.

Hereafter we denote Y0, YT0.5, YT1, YT2, YT3, YT5 for 0, 0.5, 1, 2, 3, 5 wt% respectively for nanopowders of BaTiO$_3$ addition in YBCO.

3. Results and Discussion

![Figure 1 XRD Patterns of different wt% of BaTiO$_3$ added YBCO](image)

Figure 1 shows the XRD pattern of pure and 1, 2, 3, and 5 wt% of nano BaTiO$_3$ added YBCO. In the XRD pattern of the YBCO–BaTiO$_3$ composite samples, the peaks corresponding to cubic BaTiO$_3$ could be observed at 2θ= 31.1, 42.9 and 55.14. Even upto 5 wt % of nano BaTiO$_3$ was added, the peak position of YBCO remains unaltered without any shift.

![Figure 2 SEM images of the fracture surface of the samples](image)
The SEM micrographs of the fractured surface of sintered YBCO-BaTiO$_3$ composites are shown in figure 2. The microstructure of the samples seems to improve with the increasing content of BaTiO$_3$ in YBCO. It is clearly seen that pure YBCO sample is porous with significant amount of voids of micron size, resulted a low sintered density. It is also clear from the micrographs that the porosity lowers as the percentage of addition of nanocrystalline BaTiO$_3$ in YBCO increases.

![Figure 2 SEM micrographs of the fractured surface of sintered YBCO-BaTiO$_3$ composites](image)

**Figure 3** EDAX spectrums of the YBCO-BaTiO$_3$ composites

The EDAX analysis for pure and BaTiO$_3$ added samples are shown in figure 3. The spectra indicate the presence of BaTiO$_3$ in the YBCO compound in its respective stoichiometric ratios.

![Figure 3 EDAX spectrums](image)

**Figure 4(a)** Magnetic field dependence of transport $J_c$  
(b) Variation of the normalized pinning force density ($F_p/F_{p-max}$) with applied field

Magnetic field dependence of transport $J_c$ ($J_c$-$B$ characteristics) of the samples at 77 K is shown in figure 4 (a). The $J_c$-$B$ characteristics of BaTiO$_3$ added samples are found to be much better than that of the pure sample. The samples YT0.5, YT1 and YT2 display good $J_c$-$B$ behavior in the graph, of which the YT2 exhibit the best. $J_c$ increases appreciably with increasing concentration BaTiO$_3$ from 147 MA/m$^2$ for Y0 to an optimum value of 516 MA/m$^2$ for YT2 sample and then decreases for further increasing concentration of nano additives. The obtained value for $J_c$ of YT0.5 (251 MA/m$^2$), YT1 (378 MA/m$^2$), YT2 (516 MA/m$^2$) are 70%, 150%, 250% respectively, more than that of the pure YBCO (147MA/m$^2$) sample. These characteristics show that addition of BaTiO$_3$ in optimum concentration ($x=2$ wt %) in YBCO enhances the self-field $J_c$, and gives significant improvement in the $J_c$-$B$ characteristics of the superconductor.

Using the volume pinning force density, $F_p = J_c \times B$, one can investigate the flux pinning strength of the system [5-6]. The normalized volume pinning force density ($F_p/F_{p-max}$) calculated from the data of $J_c$-$B$ characteristics as a function of the applied field is plotted in figure 4(b). It is seen that addition
of BaTiO$_3$ shifts the peak positions of $F_p/F_{p\text{-max}}$ towards higher fields. This confirms that the flux pinning strength of nano BaTiO$_3$ added samples increases significantly compared to the pure YBCO. Table 1 summarizes all the results obtained for pure and different weight percentages of BaTiO$_3$ added YBCO samples.

| Sample   | Sintering temperature (°C) | Sintered Density (g/cm$^3$) | $T_{c\text{-onset}}$ (K) | $T_{c\text{-zero}}$ (K) | Room Temp resistivity ($\mu$Ωm) | Self field $J_c$ (MA/m$^2$) | $F_{p\text{-max}}$ (x 10$^5$ N/m$^3$) |
|----------|-----------------------------|-------------------------------|--------------------------|--------------------------|-------------------------------|-----------------------------|---------------------------------|
| Y0       | 985                         | 5.53                          | 98                       | 92                       | 9.3                           | 147                         | 30                             |
| YT0.5    | 983                         | 5.68                          | 102                      | 92                       | 19.9                          | 251                         | 120                            |
| YT1      | 982                         | 5.82                          | 103                      | 92                       | 30.7                          | 378                         | 184                            |
| YT2      | 980                         | 5.88                          | 103                      | 91.5                     | 46.8                          | 516                         | 276                            |
| YT3      | 978                         | 5.86                          | 102                      | 91                       | 58.2                          | 428                         | 176                            |
| YT5      | 975                         | 5.84                          | 99                       | 90                       | 74                            | 202                         | 70                             |

The obtained results show that with the BaTiO$_3$ addition, the vortex pinning increases. The $F_p$ for the composite sample, YT2 is 9 times higher than the value of pure YBCO. Such a higher value of $F_p$ in the composite sample could be the result of BaTiO$_3$ particles acting as artificially generated pinning centers. Thus, in future possible applications, the addition of BaTiO$_3$ to Y-123 can be effective in enhancing the superconducting properties such as critical current density and pinning force in a relatively low magnetic field region below 1 T.

In our studies we conclude that the change in the intrinsic parameters and the structure defect density induced by the addition of BaTiO$_3$ could be the reason for enhanced flux pinning. The observed improvement in $J_c$ over a small range of BaTiO$_3$ content is direct evidence for the presence of effective flux pinning. The BaTiO$_3$ particles stay around outside of the grain might also act like catalyst to improve the structural quality at the grain boundaries. This in turn can causes the increase of inter-grain contact surface and increase the number of flux pinning centers at the inter-grain regions and results in the enhancement of $J_c$ even in the presence of higher magnetic field.

4. Conclusions

In conclusion, we synthesized pure YBCO and YBCO with different weight % of nano BaTiO$_3$ composite samples and systematically investigated its effect as artificially generated pinning centers. There is not much variation in transition temperatures ($T_c$) of pure and composite samples was observed while a significant enhancement in the value of $J_c$ and $F_p$ for an optimum 2 weight percentage BaTiO$_3$ added YBCO samples, relative to pure YBCO is observed. About 250% of enhancement in the value of $J_c$ is achieved in the composite sample when compared to pure YBCO, over the range of applied magnetic field. The introduction of BaTiO$_3$ nanoparticles in YBCO resulted in the increase in pinning force density from 30x10$^5$ N/m$^3$ to 276x10$^5$ N/m$^3$ at 77 K.

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