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Enhancement of the Current Density J_C for $Bi_2Sr_2CaCu_2O_8$ by Means of Carbon and $NbSe_2$ Nanotubes

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Abstract Three polycrystalline $Bi_2Sr_2CaCu_2O_8$, $Bi_2Sr_2CaCu_2O_8$ with carbon nanotubes, $Bi_2Sr_2CaCu_2O_8$ with $NbSe_2$ nanotubes were synthesized by solid state reaction method and studied by scanning electron microscopy, X-ray diffraction, magnetization measurements, and high resolution transmission electron microscopy.

The critical temperature T_C for the three compounds was about 85 K. There is an enhancement in the critical current density, J_C for samples with carbon and $NbSe_2$ nanotubes as compared with pure $Bi_2Sr_2CaCu_2O_8$. The enhancement provides evidence that *wetting* exists for the two doped samples investigated.

Keywords Superconductivity · Wetting · Nanotubes

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1 Introduction

Since the discovery of high temperature superconductivity in the cuprates [1–3] such as $YBa_2Cu_3O_{7-x}$(YBCO) and $Bi_2Sr_2CaCu_2O_8$ (BSCCO), a great deal of research has been carried out on flux pinning in these materials in order to find ways of increasing their critical current density J_C for technological applications. In order to achieve this goal, several methods had been reported in the literature such as adding impurity phases to the superconductor like $Y_2Ba_2CuO_2$ [4], columnar defects generated by ion irradiation [5], point defects generated by oxygen deficiency [6], or chemical substitution [7, 8]. In our previous work [9], we presented experimental evidence of a small enhancement on J_C by carbon nanotubes (CN) intercalation produced by irradiation in polycrystalline BSCCO samples. In this paper, we continue our quest in order to explore possible manners of increasing J_C, by adding CN produced by spray pyrolisis [10] and $NbSe_2$ nanotubes [11] on BSCCO. It had been demonstrated in one of our early studies [12] a method for embedding CN in BSCCO samples, unfortunately, by this method was impossible to predict the quantity of CN added to the BSCCO matrix. We speculated that only about 20 weight percent of the graphite used in order to create the CN by irradiation, were nanotubes. The same criterion was followed for the case of $NbSe_2$ nanotube production. Nonetheless, *wetting* by the BSCCO matrix appears as a necessary condition for enhancing flux pinning with a subsequent enhancement of the critical current density J_C. In our study, we decided instead to use a solid-state technique in order to embed the CN produced by spray pyrolisis, as well as the $NbSe_2$ nanotubes produced by irradiation into the BSCCO matrix. Morphological inspection, X-ray diffraction, and magnetization

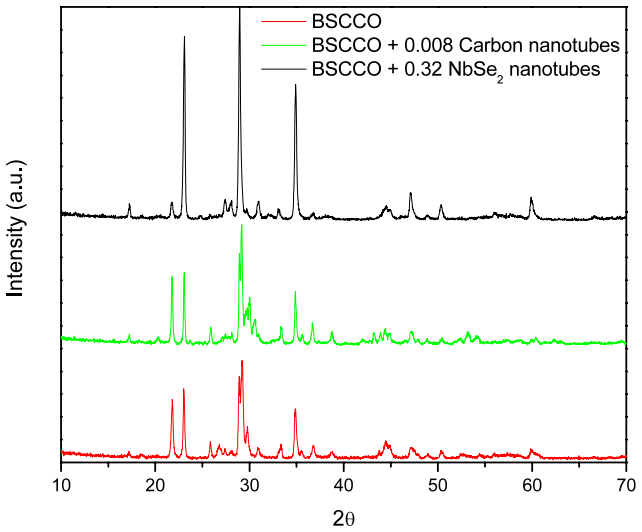


Fig. 1 X-ray diffraction patterns for pure BSCCO (*lower graph*), BSCCO plus 0.008 CN (*middle graph*) and BSCCO plus 0.32 $NbSe_2$ (*top graph*) nanotubes

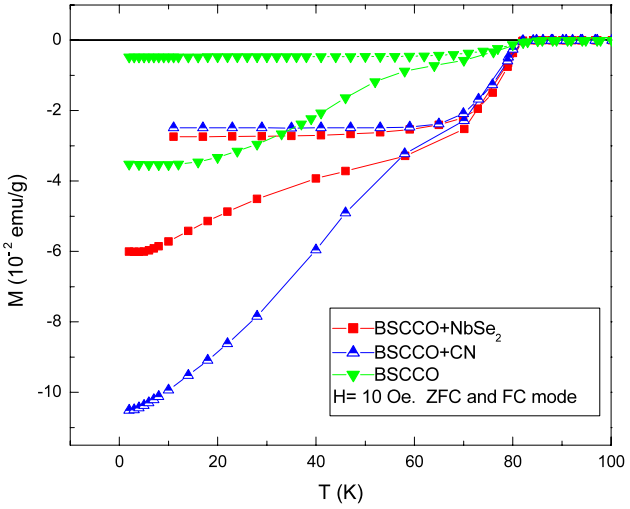


Fig. 2 Magnetization M vs temperature T for pure BSCCO, BSCCO + CN and BSCCO + $NbSe_2$ nanotubes, respectively

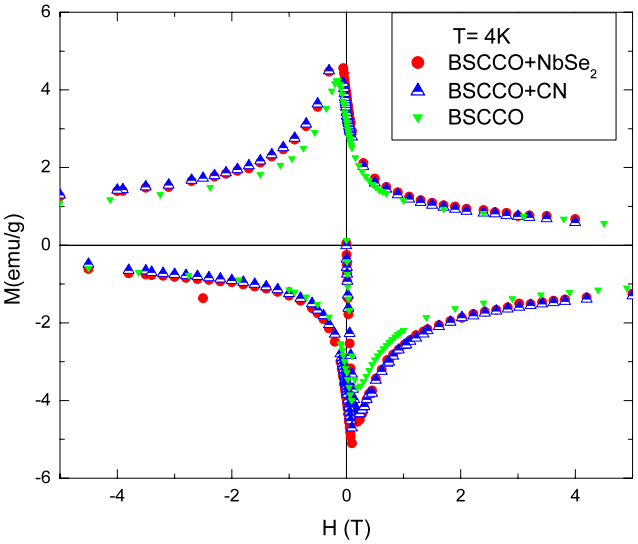


Fig. 3 Magnetization M vs magnetic field H isotherms at $T = 4$ K for the three samples

measurements were performed in order to ascertain the *wetting* effect (CN and $NbSe_2$ nanotubes) on J_C in the BSCCO superconductor compound. It is important to mention that this work is the first study of the enhancing of J_C when $NbSe_2$ nanotubes are added into the BSCCO (2212) phase.

2 Experimental Details

The BSCCO samples were prepared by means of solid-state reaction techniques as was reported by our group [9]. Also, the CN produced by spray pyrolisis have been reported by Galvan et al. [10]. This selected preparation method was used because the nanotubes are formed in a highly dense concentration and growing in a specific direction, which make them suitable to be used for our purpose of embedding them into the BSSCO matrix.

One of the questions which we did not consider in our former investigation on the same subject was related to the *real* quantity of CN added to the BSCCO sample. Accordingly, we performed a statistical analysis on different samples and different areas of the CN produced by pyrolisis [9]. With this method, it is estimated that about 90% of the complete area was CN. On the other hand, in $NbSe_2$ nanotube samples produced by irradiation, as explained before only about 20% of the total analyzed area were nanotubes.

Three pellets of the BSCCO powders were made: Pure BSCCO, BSCCO with CN, and BSCCO with $NbSe_2$ nanotubes. Afterwards, the three pellets were subjected to a heat treatment for 300 °C/5 hours with subsequent heating for 650 °C/10 hours in flowing Ar which allows for a good *wetting* contact between the nanotubes and the BSCCO matrix as reported by Fossheim et al. [13]. A subsequent oxygen heat treatment at the same temperature and time was performed in order to optimize the superconducting properties of the sample.

Scanning Electron Microscopy (SEM) measurements were performed on a JEOL–JSM 300 microscope for each sample in order to analyze the morphologic characteristics of the composite material; furthermore, phase identification for each sample was carried out using X-ray diffraction measurements with a Philips XRD/X'PERT diffractometer using Cu K_α radiation at a voltage of 40 KV and a current of 45 mA.

Table 1 Superconducting critical temperature T_C, average grain size, average width of the hysteresis loop (at $H = 4T$), density and average intergranular critical current density J_C at 4 and 10 K for pure BSCCO, BSCCO + CN and BSCCO + $NbSe_2$ nanotubes

Material	T_C (K)	Grain size (μm) $b \times a$	Average ΔM (emu/gm)	Density (gm/cm^3)	Average J_C (MA/cm^2) 4 K	Average J_C (MA/cm^2) 10 K
Pure BSCCO	≅ 85	2.4 × 6.6	2.8 (4 K) 1.06 (10 K)	6.54	1.73 ± 0.33	0.65 ± 0.18
BSCCO + CN	≅ 85	1.9 × 3.8	2.96 (4 K) 1.25 (10 K)	6.54	2.46 ± 0.57	0.91 ± 0.29
BSCCO + $NbSe_2$–N	≅ 85	1.4 × 4.7	2.88 (4 K) 1.13 (10 K)	6.54	4.12 ± 0.59	1.62 ± 0.53

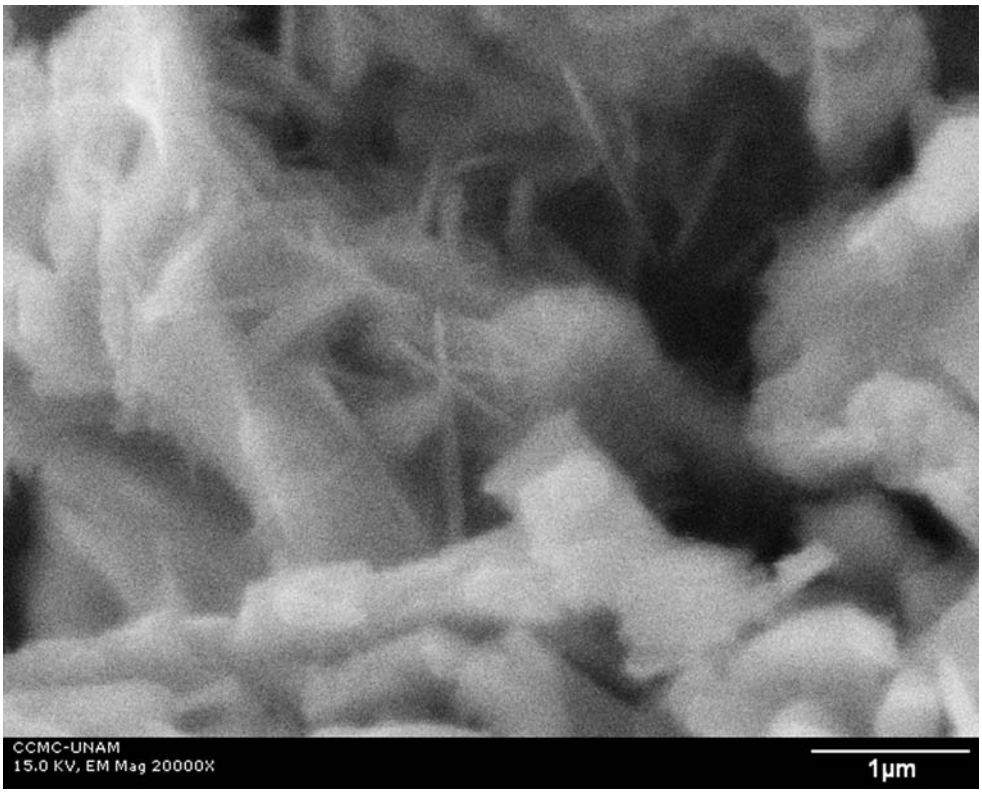


Fig. 4 4 SEM micrograph for BSCCO with carbon nanotubes. Notice the CN immersed into the BSCCO matrix

Magnetization measurements were performed on rectangular samples with 5 × 3.0 × 1.2 mm dimensions using a *Quantum Design MPMS-5S* and a *MagLab2000* magnetometers.

BSCCO samples (with CN and $NbSe_2$ nanotubes) were pulverized and dispersed in ethanol. A droplet of this suspension was deposited on a holey silicon oxide supported in copper grids for transmission electron analysis (TEM). The samples were analyzed with the aid of a JEOL 2010 F microscope equipped with a Schottky-type field emission gun, ultra-high resolution pole piece ($Cs = 0.5$ mm), operating at 200 kV. A Gatan CCD camera was used for image acquisition.

3 Results and Discussion

In order to detect any possible changes in the unit cell of the BSCCO matrix, X-ray diffraction was performed on each sample. X-ray patterns for pure BSCCO (lower figure), BSCCO plus 0.008% weight percent of CN (middle figure) and BSCCO plus 0.32% weight percent $NbSe_2$ (top figure) nanotubes are provided in Fig. 1. Comparing the BSCCO plus CN with pure BSCCO as has been reported by Namgung et al. [14] corresponding to PDF card No. 00-041-0317 from the International Centre for Diffraction Data, [the 22° corresponds to (0 0 8), the 23° corresponds to (1 1 3), the 29° corresponds to (1 1 5), while the 35° corresponds to (0 2 0) reflective planes, respectively]. It is possible to observe a perfect match between all the diffraction peaks,

except for a small shoulder located at about 29° in pure BSCCO that has been changed in the BSCCO plus CN. On the other hand, when a comparison has been performed on the BSCCO plus $NbSe_2$ with pure BSCCO, a difference is observed at about 22°. This peak is reduced in the BSCCO plus $NbSe_2$ nanotubes. Moreover, the peak located at 29° in pure BSCCO, is formed by a multiplete, while in the BSCCO plus $NbSe_2$ nanotubes has been changed to a single peak. This may indicate that a change has occurred in the original unit cell due to the inclusion of the CN or $NbSe_2$. We speculate that certain amount of CN has been embedded into the BSCCO matrix, although in order to prove this asseveration, a more careful analysis like HRTEM, should be performed and will be explained letter on this investigation.

Figure 2 yields magnetization M *vs.* temperature T for pure BSCCO, BSCCO with CN and BSCCO with $NbSe_2$ nanotubes, respectively. $M(T)$ measurements were from 2 to 120 K, in a zero-field (ZFC) and field cooling (FC) modes, under a magnetic field intensity of 10 Oe. The resulting superconducting transition temperature for the three samples was $T_C = 85$ K.

Magnetization M *vs* magnetic field H isotherms at $T = 4$ K for the three samples enunciated in the former paragraph are provided in Fig. 3. The hysteresis loops are reminiscent of typical high T_C superconducting samples. There, BSCCO plus $NbSe_2$ increases the area hysteresis loop, as compared with pure BSCCO. The experimental critical current density, J_C for each sample can be obtained using Bean critical state model [15, 16]. For rectangular parallelepiped samples [17], the following equation is used:

$$J_C = 20\Delta M/[b - b^2/3a], \tag{1}$$

where a and b are superconductor grain dimensions which were considered to be transverse to the direction of the magnetic field applied, also, $b > a$, ΔM is the magnetization difference between increasing and decreasing field branches taken from the hysteresis loop and is obtained from $M(H)$ data of Fig. 3. As ΔM was measured in emu/gm and in order to be used in (1) should be converted to emu/cm^3 of the selected sample, hence, it will be necessary to know weight percent as well as the theoretical density for BSCCO, which was provided in our former investigation [9].

Grain size dimensions in the superconducting material, a and b were obtained from SEM measurements, and a statistical study was performed in different areas of each sample separately. Figure 4 shows a SEM micrograph for BSCCO with CN. Notice that the nanotubes emerge from the BSCCO matrix which assess that there is a true *wetting* in which they are embedded. The values for T_C obtained from Fig. 3, average grain size, ΔM, density, and J_C are provided in Table 1.

The value of the critical current density J_C at 4 K reported for pure BSCCO was 1.73 ± 0.33 MA/cm^2, while

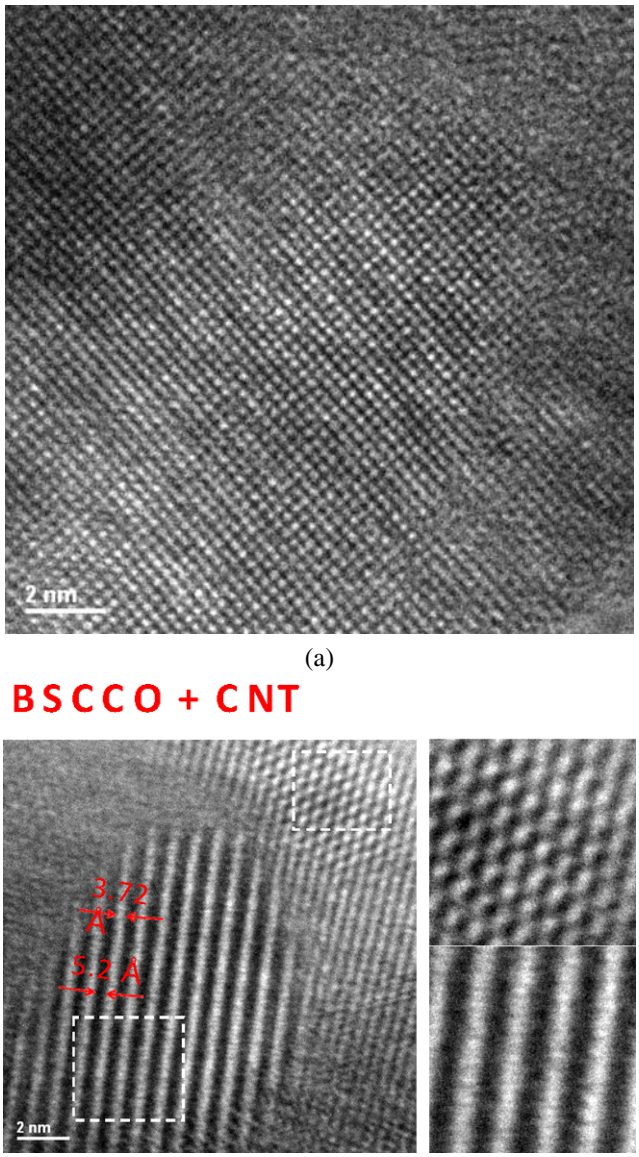
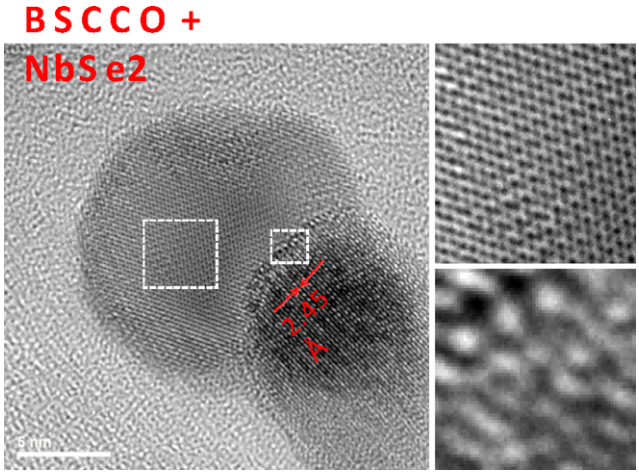


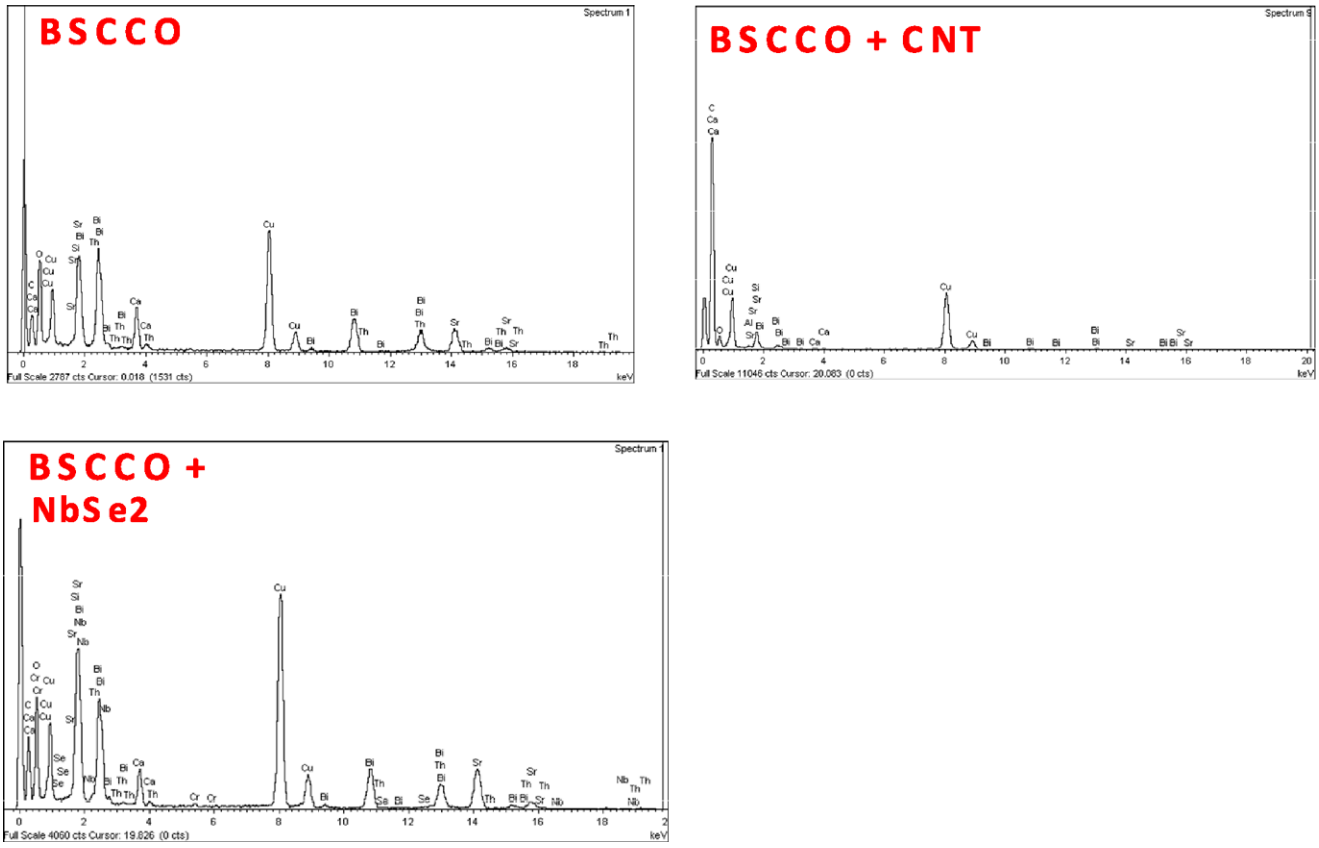
Fig. 5 (**a**) to (**c**) High Resolution Transmission Electron micrograph for pure $Bi_2Sr_2CaCu_2O_8$, $Bi_2Sr_2CaCu_2O_8$ plus carbon nanotubes and $Bi_2Sr_2CaCu_2O_8$ plus $NbSe_2$ nanotubes. (**d**) EDX for the samples mentioned above, notice that only the compounds for BSCCO, CN and $NbSe_2$ are shown

for BSCCO with CN the J_C value reported was 2.46 ± 0.57 MA/cm^2 and for BSCCO with $NbSe_2$ nanotubes the critical current density value reported was 4.12 ± 0.59 MA/cm^2. Notice there has been a steady increment on J_C when CN (1.42 time the BSCCO value), as well as $NbSe_2$ (2.38 times the BSCCO value) nanotubes had been added to the BSCCO samples.

In addition, the values for the critical current at 10 K for pure BSCCO was 0.65 ± 0.18 MA/cm^2, while for BSCCO plus CN the value obtained was 0.91 ± 0.29 MA/cm^2 and



(c)



(d)

Fig. 5 (*Continued*)

for BSCCO plus $NbSe_2$ nanotubes the reported J_C was 1.62 ± 0.53 MA/cm^2.

Furthermore, there has been a steady increment on J_C when CN (1.42 times BSCCO value), as well as when $NbSe_2$ (2.49 times BSCCO value) had been added.

An important result of this study is the steady increment on J_C when carbon nanotubes were added to the BSCCO. The increase observed, respect to pure BSCCO, and was 1.42 times the BSCCO value, whereas for BSCCO plus $NbSe_2$ the increase was 2.38 times the BSCCO value. It is worth mentioning that the experimental error in the measurements, are small numbers, which might provide an indication that the samples are homogeneous. Nevertheless, the most important point is the J_C increase for BSCCO plus

$NbSe_2$ nanotubes sample. This effect indicates the appropriated *wetting* in the BSCCO matrix and that the metallic nature of $NbSe_2$ has a profound effect in the vortex pinning. The immediate question arises about if the influence of the superconducting state of $NbSe_2$ is important or not on J_C enhancement. This was proved by performing isothermal magnetic measurements below and above the transition temperature, in Table 1, we show that the enhancement of the critical current density follows a normal trend of decreasing when T was 10 K (above T_C of $NbSe_2$ [19]). This result seems to confirm that the metallic nature of the $NbSe_2$ wetting the BSCCO matrix increases the vortex pinning, and consequently increasing the J_C. Lastly, we have to remember that producing carbon nanotubes for any method known today gives an average of about one-third of metallic nanotubes of the total production. The nonmetallic or insulating form of carbon nanotubes accordingly, may deleterious to a vortex pinning effect.

HRTEM images taken on pristine BSCCO and BSCCO with CN as well as BSCCO plus $NbSe_2$ are shown on Figs. 5(a) to (c). Figure 5(a) provides a HRTEM micrograph for pure $Bi_2Sr_2CaCu_2O_8$ phase. Moreover, Fig. 5(b) yields a HRTEM micrograph of a sample composed of BSCCO plus CN. Notice that in the same micrograph it is possible to locate two different crystallographic arrangements corresponding to BSCCO and Bi–O planes located within the BSCCO crystal. On the right side of the figure are the reconstructed images obtained from the corresponding Fourier transforms generated in the selected regions, as marked with dotted lines. Furthermore, Fig. 5(c) corresponds to a HRTEM micrograph for BSCCO plus $NbSe_2$ nanotubes. Notice that in the same micrograph we can isolate two distinct areas, one corresponding to BSCCO while the intermediate phase resembles to the one dimensional morphology observed in nanotube structures. Figures 5(d) yield the EDS analysis for the samples mentioned above. Notice that only Bi, Sr, Ca, Cu, C, Nb, and Se are shown in the corresponding figure, providing indication that those elements are present for each case.

4 Summary

We have investigated the inclusion of CN made by pyrolisis into the BSCCO matrix providing evidence that *wetting* exists with an enhancement of 1.42 times the original value of J_C from the pure BSCCO (at 4 K). Moreover, we reported for the first time to our knowledge, the inclusion of $NbSe_2$ nanotubes produced by irradiation into the BSCCO matrix with a reported enhancement of 2.38 times the original value of J_C of the pure BSCCO (at 4 K) and an indirect evidence for the existence of *wetting*. The enhancements obtained for the two systems provide indication that the method could be considered a plausible way to increment the critical current density in superconductors like BSCCO and use them in industrial applications. Moreover, there is no decrement in the critical temperature for the two systems considered which a beneficial factor is obtained. X-ray analysis provides evidence that some kind of change had occurred in the original unit cell of the BSCCO matrix, although in order to provide a clear evidence of *wetting* a HRTEM analysis should be performed. Our HRTEM analysis is preliminary and we expect to continue with our investigation in order to provide more conclusive evidences of this process.

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