Chapter-IV

Superconducting properties of YBCO Nanocomposites

4.1. Introduction

In the earlier chapter we had discussed the macro- and microstructures of IG processed YBCO with ceria, zirconia and Ba-Ce-O additions. Dramatic differences were observed in the macro- and microstructures based on the nature of the additives and their concentration. In this chapter, we present results of current density measurements on the above samples and attempt to correlate them to the observed microstructures.

4.2. Superconducting properties of Ceria dope YBCO nanocomposites

The current densities \( J_c \) supported by the samples Ce-2, Ce-5 and Ce-10 (see Section 3.2 of Chapter III, for an explanation of the nomenclature) as a function of applied magnetic field, were estimated from magnetic hysteresis loops recorded at different temperatures using a PPMS facility.

The \( J_c(H) \) obtained in samples Ce-2, Ce-5 and Ce-10 at 65 K and 77 K are shown in Figs. 4.1 (a) and (b) respectively. The Ce-10 sample shows the best performance and Ce-5 the worst. Since, the observed variation in \( J_c(H) \) is not systematic with ceria content; we have repeated the complete experiment and confirmed that such an anomalous \( J_c(H) \) behavior of the Ce-5 sample is reproducible.
Fig. 4.1. $J_c$ is plotted against applied magnetic field for the samples Ce-10 (red), Ce-2 (blue) and Ce-5 (green) at (a) 65 K, and (b) at 77 K.

The $J_c$ versus H, $(J_c(H))$ curves, obtained in the Ce-10 sample at different temperatures are plotted in Fig. 4.2. We note that the current densities observed in the sample do not decay substantially even up to 9 T at 77 K. The observation of flat $J_c(H)$ to high fields at 77 K is similar to that reported in the un-doped POIGP (Ce-0) sample which showed a zero field $J_c$ of 19 kA/cm² at 77 K [1].

Fig. 4.2. Critical current density versus applied magnetic field is plotted for the Ce-10 sample at different temperatures.
It has been proposed [2] that the current density obtained in superconducting samples can be correlated to the size of the flux pinning defects occurring in them, as per the following equation:

\[ H_p = \frac{2\phi_0}{\sqrt{3}(a_r)^2} \]  

where \( H_p \) is the peak field at which the maximum pinning occurs, \( \phi_0 \) is the flux quantum and \( a_r \) is the vortex lattice spacing.

It has been proposed that the observed high current density in the POIGP samples to high fields is a result of flux pinning defects occurring in the sample spanning wide size ranges [1]. The high values of \( J_c \) near 9 T in Ce-0 sample was correlated to the occurrence of wide spread twinning in the Y-123 matrix. Such twins were observed by FESEM. Their presence was also revealed by EBSD. The EBSD also suggested that the occurrence of fine defects around the Y-211 particles was associated with dense distribution of fine Y-211. Transmission electron microscopy studies [3] on the Ce-0 sample revealed the presence of still finer defects \( \sim 15 \) nm starting at the twin boundaries. The Ce-10 and Ce-2 samples show \( J_c \) values almost independent of \( H \) up to 9 T at 65 K, just as the Ce-0 sample. This might be correlated with the fine grain (\( \geq 0.5 \) \( \mu \)m) size of the Y-211 and a narrow distribution in Y-211 size in Ce-10, shown in Fig. 3.11. Similar microstructure but with a Y-211 distribution in larger size range (\( \geq 1 \) \( \mu \)m) was observed in Ce-2 sample. Fig. 4.3 shows twinning in all the CeO\(_2\) doped samples. Absence of macro defects and presence of homogeneously distributed Y-211 and nanoparticles and the resultant twinning in Ce-2 and Ce-10 samples account for the observed flat \( J_c \), being almost independent of \( H \) up to 9 T at 65 K. Further discussion can be found in section 4.4.
Fig. 4.3. Twinning is observed in all CeO$_2$ doped YBCO nanocomposites (Ce-2, Ce-5 and Ce-10).

The electrical resistivity and ac susceptibility of the samples Ce-2, Ce-5 and Ce-10 were measured as a function of temperature following the procedures discussed in Chapter II, Section 2.6. and 2.7.1. The results are shown in Figs. 4.4 (a) and (b) respectively.

Fig. 4.4. (a) The electrical resistivity, and (b) the real part of ac susceptibility of the samples Ce-10 (red), Ce-2 (blue) and Ce-5 (green) are plotted with respect to temperature.
A shift in the diamagnetic transition to below 92 K and considerable width of the transition in $\chi'$ vs. T can be observed predominantly in Ce-2 and Ce-5. An examination of the curves, in Fig. 4.4, show that in the Ce-10 sample, there is a considerable amount of Y-123 phase with $T_c$ close to 92 K, whereas in Ce-2 and Ce-5 samples, substantial part of the material consists of lower $T_c$ phases. This can possibly be attributed to the dissolution of Ce in the Y-123 phase forming solid solutions having lower $T_c$.

In Fig. 3.20 of Chapter III, it was observed using elemental mapping that the outer regions of the Y-211 grains contained ceria. Such regions dissolve in the liquid phases to generate a matrix of Y-123 containing some amount of cerium. Cerium substitution in Y-123 lowers the $T_c$ as can be seen in Fig. 4.5 [4].

![Figure 4.5](image)

**Fig. 4.5.** The figure shows that the addition of ceria and Pt to Y-123 lowers its superconducting transition temperature [4]. The effect is less pronounced with Pt addition, and this suggests that the $J_c$ of Pt-containing samples are likely to be seriously affected by the additive. We note by comparing the present figure with Figs. 4.4 (a) and (b) of measurements in our samples that the Ce-10 sample retains considerable volume of Y-123 without ceria dissolution. It might be noted from Fig. 3.6 that the ceria nanoparticles in the preform used for the fabrication of the Ce-10 sample grow into much fewer number of nano-rods, which get converted to barium cerate particles during the IG process. This leads to localization of ceria distribution in the Y-123 matrix of the Ce-10 sample.
Ce was detected by elemental mapping in the Y-123 phase in the regions close to the Y-211 grains. The lower current densities observed in the Ce-2 sample in comparison with the Ce-10 sample, and the relatively lower current densities of both the Ce-10 and Ce-2 samples in comparison with the Ce-0 sample, might be attributed to the presence of significant amount of low Tc phase containing cerium dissolution in the 123 phase.

The difference in the behavior of the Ce-5 sample can be traced to the nature of the preform used in fabricating it. The SEM micrographs of Y-211 preforms with varying amounts of ceria nanoparticles, after 4 h at 950 °C, are reproduced from Chapter III (Fig. 3.6) in Fig. 4.6 for convenience of discussion.

**Fig. 4.6.** The micrographs in the top row show from left to right, the preforms used in the fabrication of the Ce-2, Ce-5 and Ce-10 samples, respectively. The preform used in the fabrication of the Ce-2 sample has the least amount of ceria and retains its porosity. In the preform used for the fabrication of the Ce-10 sample, the porosity
is retained because the ceria nanoparticles fuse among themselves to form ceria nano-rods. In the preform used in the fabrication of the Ce-5 sample, the Y-211 particles have fused together in the presence of ceria, eliminating continuous porosity needed for liquid phase entry.

It can be observed that the preforms with 2 and 10 wt. % of ceria nanoparticles have enough porosity to facilitate infiltration of liquid phases during the IG process, but in the preform with 5 wt. % ceria nanoparticles, the Y-211 particles are nearly fused blocking the entry of liquids. As schematically shown in Fig. 4.6, the sample with 10 wt. % of ceria is able to retain porosity because of the tendency of the ceria particles to grow into nano-rods, a few hundreds of nanometers long, with a diameter of 40-60 nm. The formation of the nano-rods makes the preform porous.

The mechanism proposed above for the difference in the behavior of the Ce-5 sample is supported further in Fig. 4.7. In the Infiltration Growth experiments, a Y-123 pellet, which served as a source of liquid phases, was kept on top of the Y-211 preform. After the liquids infiltrate the preform at a few tens of degrees above the peritectic formation temperature of Y-123, the Y-123 pellet would shrink considerably. This is shown schematically in Fig. 4.7 (a). In Figs. 4.7 (b) and (c), we show the Ce-10 sample after the IG process. It can be observed that the Y-123 pellet on top has shrunk considerably and the Y-211 pellet retained has its size as expected. In Figs. 4.7 (d) and (e), it can be seen that in the case of the Ce-5 sample, there is not much shrinkage of the Y-123 pellet. This shows that the liquid phases were unable to infiltrate into the Y-211 preform in this case due to the fused Y-211 particles reducing its porosity.
Fig. 4.7. (a) A side view of the arrangement used in the IG process is shown schematically. After melting and infiltration of the liquid phases into the Y-211 preform the 123 pellet shrinks. In (b) and (c) the side and top views respectively, of the Ce-10 sample are shown after IG processing. The observed shrinkage in the top Y-123 pellet is due to infiltration of liquid phase from Y-123 into the Y-211 preform, can be observed. (d) and (e), which show the side and top view respectively of the Ce-5 sample demonstrates the fact that the Y-123 pellet had not shrunk after the experiment suggesting that the entry of liquid phases into the Y-211 preform was blocked in this case.

Fig. 4.8 shows the FE-SEM image of the Ce-5 sample in comparison with those of the Ce-2 and Ce-10 samples at the same magnification. It is observed from the low magnification picture of the Ce-5 sample that there is considerable amount of macro-porosity occurring as a result of improper infiltration. On the other hand the Ce-2 sample shows very little porosity, and the Ce-10 sample, almost none at all.
Fig. 4.8. It can be observed that there are very few macroscopic defects in the (a) Ce-2 sample and (c) the Ce-10 sample. (b) Large areas with macroscopic defects can be observed in the Ce-5 sample due to improper liquid phase infiltration.

Table 4.1 summarizes the information on the defect sizes in the samples Ce-2, Ce-5 and Ce-10. It can be observed from the Table that Ce-5 sample shows the maximum amount of porosity and also the maximum values for the inter platelet gaps. The size and quantum of defects then decrease in the order Ce-2 to Ce-10. The superconducting performances of the samples also decrease in the same order.

<table>
<thead>
<tr>
<th></th>
<th>Y-211 Avg. size</th>
<th>Porosity (%)</th>
<th>Platelet width</th>
</tr>
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<tbody>
<tr>
<td>Ce-2</td>
<td>~1-2 µm</td>
<td>~7</td>
<td>2-5 µm</td>
</tr>
<tr>
<td>Ce-5</td>
<td>~1 µm</td>
<td>~16.5</td>
<td>10 µm</td>
</tr>
<tr>
<td>Ce-10</td>
<td>0.5 µm</td>
<td>~1.5</td>
<td>~500 nm</td>
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4.3. Flux pinning force

Flux pinning forces ($F_p$) [5] are calculated from the $J_c$ vs. $H$ graphs at 65 K and 77 K for the Ce-2, Ce-5 and Ce-10 samples, using the following equation

$$F_p = J_c \times \mu_0 H \quad (4.2)$$

$F_p$ is plotted as function of the applied field at 65 K and 77 K in Figs. 4.9 (a) and (b) respectively.
The flux pinning force in the Ce-10 sample which has extremely fine Y-211 grains and also wide-spread twinning, shows very high levels of flux pinning in comparison with the Ce-2 and Ce-5 samples, and the flux pinning in the Ce-10 sample peaks at relatively high magnetic fields at 65 K and in a broad range of fields at 77 K.

4.4. Flux profile studies

In the discussion of the observed $J_c(H)$ of the Ce-2, Ce-5 and Ce-10 samples in the above section, we observe that the $J_c(H)$ is strongly dependent on macroscopic features such as porosity and other kind of defects like platelet gaps, which might be considered as weak-links. Experiments on flux penetration into the sample on application of magnetic field would be of interest in exploring the role of such weak-links on the $J_c(H)$ of the sample. The experiment consists of applying a dc field (in the order of Teslas) and then studying the flux penetration into the sample by using an ac field as a probe. In order to understand flux penetration at various dc fields into the present samples, flux penetration depths were calculated from the real part
of ac susceptibility measured in the Ce-10 and Ce-2 samples with increasing amplitude of ac field. Flux penetration depth \( \frac{p}{R} \) is determined using the formula suggested by Campbell [6], which is given below

\[
\frac{p}{R} = 1 - \sqrt{-\frac{1}{k} \frac{dS}{dH_{ac}}} 
\]

\[ \text{(4.3)} \]

\( \frac{p}{R} \) is the normalized penetration depth where \( R \) is the radius of a cylindrical sample and \( p \) is the depth to which magnetic field has penetrated. An external dc field \( (H_{dc}) \) and a small superimposed ac field \( (H_{ac}) \) parallel to the longest axis of the sample are applied. The induced signal in the secondary coils (with one of the two coils containing the sample) is fed to a lock-in amplifier and the in-phase signal \( (S) \) is measured as a function of ac field amplitude.

The above experiments were carried out at 77 K using the PPMS facility. In Fig. 4.10, we plot the variation in \( \frac{p}{R} \), computed using Eq. 4.3, against the ac field amplitude for the Ce-10 sample at different applied dc fields which exhibit different lines shifted along the \( \frac{p}{R} \) axis. The intercept of the lines on the \( \frac{p}{R} \) axis gives \( p_0/R \) which is a measure of reversible fluxoid motion through the sample discussed in literature [7]. The entry of flux into voids and cracks contributes to a finite \( p_0/R \), which is a shift along the \( p/R \) axis. In textured high \( J_c \) superconductors there are different types of weak-links like domain boundaries, platelet gaps, and presence of low \( T_c \) phases in the path of shielding current loops. Flux enters these weak-links at different applied field strengths depending on the distribution and nature of the weak-links and their \( J_c \). In a sample containing superconducting materials of varying \( T_c \), such ‘voids’ might also be constituted by regions of the sample gone normal at the applied dc field. Regions of stronger flux pinning do not contribute to reversible fluxoid motion or shift along \( p/R \) axis. This causes a
continuous variation of $p_o/R$ with increase in dc field. A finite value of $p_o/R$ under a constant dc field suggests that the flux has already entered the sample to a finite depth and application of ac field induces further entry as described by the lines shown in Fig. 4.10 for Ce-10 sample.

**Fig. 4.10.** A plot showing Normalized magnetic flux penetration depth ($p/R$) into the Ce-10 sample on the X-axis, with the applied ac magnetic field on the Y-axis. The graphs correspond to observations at various applied dc fields, from 0 to 8 Tesla towards the right. R is the radius of the sample; p is the depth to which the magnetic flux penetrates into the sample.

In Figs. 4.11 (a) and (b), we compare the variation in $p_o/R$ with the dc field strengths for the Ce-10 and Ce-2 samples, respectively. Distinct changes in the slope can be observed in both the figures. A slope change suggests that the flux is starting to enter a different region in the sample with a different $J_c$. In Ce-10, (Fig. 4.11 (a)), at low applied dc fields (0 - 0.5 T), the flux penetrates into ~2 % of the sample, suggesting a low $J_c$ region that allows flux
penetration at low fields. At higher dc fields (0.5-7 T), the flux continues to enter into weak-link regions of higher J_c, penetrating up to 20 % of the sample. Beyond 7 T, there is a further slope change indicating much slower flux entry between 7–9 T, with an increase from 20 to 22 % of the sample penetrated by 9 T. In contrast, in the Ce-2 sample, Fig. 4.11 (b) shows only one slope change at low fields, and the flux entry is much more and is up to 36 % of the sample at 9 T. An understanding of this behavior is attempted in comparison with the microstructural features observed in Figs. 4.12- 4.13, recorded at different magnifications.

The initial high slope regions in the p_0/R versus H_{dc} plot, indicating easy entry of flux, and observed at low fields, might be associated with flux penetration into regions such as cracks and voids. Flux penetration up to 6 % in Ce-2, in contrast to 2 % in Ce-10, can be correlated to the higher porosity levels in Ce-2 sample as can be seen in Figs. 4.12 and 4.13.
Fig. 4.12. FESEM micrographs obtained on Ce-2 and Ce-10 samples at a magnification of 500 X, shows macro defects such as pores, cracks etc. In Ce-2, large pores (~5 μm) and cracks can be seen almost through the entire field of view in the sample accounting for nearly 5-7 % of macro defects, whereas in Ce-10, very fine pores and cracks are seen accounting for a smaller percentage (1.5-2 %) of macro defects.

The region between 0.5 and 9 T for Ce-2 in Fig. 4.11 can be associated with progressive flux entry into the lower $T_c$ region, more of which turns normal with increasing dc field, and increases to 40 % of the sample at 9 T. Amount of lower $T_c$ phases is considerably large in Ce-2 compared to Ce-10 as was seen in Fig. 4.4 (b). In the case of Ce-10, the lower $T_c$ phases are less in volume in comparison with the high $T_c$ component, and this accounts for the lower flux penetration of 22 % into Ce-10 at 9 T. Much slower rate of flux entry between 7 T to 9 T in the Ce-10 sample is possibly associated with flux entry into the high $T_c$ (~92 K) matrix seen only in the Ce-10 sample (see Fig. 4.4).
Fig. 4.13. Micrographs shown in the upper row are obtained at a magnification of 5000 X for both Ce-2 and Ce-10 samples. Ce-2 shows platelet cracks which are not seen in Ce-10. The micrographs shown below are obtained at a magnification of 20,000 X for Ce-2 and Ce-10; they show large platelet gaps in Ce-2, and very fine platelet gaps in Ce-10 and most of the platelet gaps in Ce-10 are fused.

In Fig. 4.14, the $J_c(H)$ of the IG processed Y-123 sample containing 10 wt. % zirconia nanoparticles is plotted in comparison with that of the Ce-10 sample. The performance of the Zr-10 sample is poor; and the performance of samples containing lower amounts of zirconia were even poorer. It is evident from the microstructures of the samples in Fig.3.9, that the poor performance of the zirconia containing samples might be attributed to excessive Y-211 grain growth at the preform formation stage. This had made it difficult for
the liquid phases to enter uniformly into the preforms leading to large grain growth for the Y-211 phase.

![Graph](image1)

**Fig. 4.14.** $J_c$ versus H of the IG processed Y-123 sample containing 10 wt. % zirconia nanoparticles is plotted in comparison with that of the Ce-10 sample, at 77 K.

In Fig. 4.15, we plot the critical current densities obtained in the samples containing 0.1 wt. %, 0.5 wt. %, 3 wt. % and 10 wt. % Ba-Ce-O nanoparticles.

![Graph](image2)

**Fig. 4.15.** Variation of $J_c$ with H at 77 K, in YBCO composites fabricated from preforms containing various amounts of Ba-Ce-O nanoparticles; 0.1 % (green), 0.5 % (blue) 3 % (dark blue) and 10 % (red) in weight with respect to Y-211.
It might be recalled from Fig. 3.26 (reproduced in Fig. 4.16) that the sample with the smallest amount of Ba-Ce-O had the least favorable microstructure to support high current densities; the sample had large Y-211 grains generating isolated colonies of short Y-123 platelets in different orientations. By comparing with the preform microstructure, we had concluded that the particle refinement caused by small amounts of Ba-Ce-O was not sufficient to bring down Y-211 sizes substantially. In samples with higher Ba-Ce-O content, we find that, with increasing Ba-Ce-O content, the Y-211 size becomes more and more refined and the grain structure of the Y-123 with long parallel platelets is restored back in the case of Ba-Ce-O-10, which also showed better performance in field dependence of $J_c$.

**Fig.4.16.** FESEM micrographs obtained on YBCO samples with 0.1 %, 0.5 %, 3 % and 10 % of Ba-Ce-O nanoparticles at a magnification of 2,000 X.
4.5. Conclusions

Melt processed YBCO containing Pt, CeO₂, ZrO₂ and BaCeO₃ have been widely studied because of the ability of these additives to considerably refine Y-211 grain size in the final product [8-11]. The grain size refinement is expected to result in enhanced current densities in the materials. However, the observed results were not absolutely systematic with the dopant concentration and there were considerable differences based on the processing route. For instance, in the samples differently processed in the presence of Pt, grain refinement of Y-211 was observed in some cases and was not observed in some other cases [8]. It was observed that in the samples where the initial processing led to Y-211 grain growth, Pt was not effective in reducing the Y-211 size later on. Also, the current densities reported in the samples are widely scattered based on the processing route.

In experiments reported in the present thesis, we find that even very small amounts of ZrO₂ and Ba-Ce-O additives cause substantial deterioration in the current densities in comparison with that obtained in undoped IG processed samples. A dramatic effect is observed in the sample containing only 0.1% of Ba-Ce-O; in this case the microstructure of the IG processed sample gets close to that of a sintered sample and the current densities drop to very low levels. The additives, when present in larger amounts, improve the current densities supported by the samples substantially. These observations can be explained by the fact that, even with very small amount of these additives, Y-211 particles in the preform fuse leading to considerable Y-211 grain growth. The effect of more amounts of additives is to divide the Y-211 grains into smaller particles by a process discussed in Chapter-III. The fusing and grain growth of Y-211 can also affect the liquid phase entry into the preforms and affect the performance of the samples. The behavior of the
sample containing 2 wt. % of ceria was somewhat different; in this case
reaction between Y-211 grains and their fusing in the preform was not as
much as in other samples. Therefore, $J_c$ versus $H$ for Ce-2 samples was
relatively better. The Ce-10 sample also did not lose porosity in the preform
because of the formation of ceria nano-rods; thereby the infiltration of liquid
phases into the preform was good, and also the starting grain size of the Y-
211 particles were close to that of particles in the powder used, i.e. ~1 µm.
Hence, the Y-211 particles in IG processed Ce-10 sample were much smaller
than in the Ce-0 sample, i.e. in the IG processed sample without any additives.
It might be noted that a Y-211 distribution finer than what is obtained in the
Ce-10 sample has not been generated in MG or IG processed samples until
now. We observe that the current densities in these samples remain flat up to
9 T magnetic field and the irreversibility field is better than 9 T at 77 K. This
is attributed to the presence of the very fine second phase particles present
in it and because of extensive nano-twinning. However, in spite of
substantial refinement of Y-211, there is no remarkable improvement in $J_c$ in
Ce-10 sample over that in the Ce-0 sample.

The lowered $J_c$ in the doped samples, in spite of a ‘favorable’
microstructure, might turn out to be a difficult problem to solve; it results
from lower $T_c$ of the Y-123 phase with the dopant dissolved in it. It is
therefore likely that the method that we have developed in this thesis to
distribute nanoparticles individually and separately in the preform will be
more attractive in the case of nanoparticles which do not react with Y-211 or
Y-123; an example would be nanoparticles of Gd-211 and NbO$_3$ which have
been introduced into melt processed NEG-123 system to dramatically
improve its $J_c$, as discussed in the literature [12].
References


