CHAPTER V

ELECTRICAL TRANSPORT AND PERCOLATION STUDY IN YBa$_2$Cu$_3$O$_{7.5}$ - REBa$_2$HfO$_{5.5}$ SUPERCONDUCTOR- INSULATOR COMPOSITE

V.1 Introduction

The chemical non-reactivity of REBa$_2$HfO$_{5.5}$ materials with YBCO superconductors indicate their potential as substrates for YBCO films. In order to confirm their chemical compatibility with YBCO, it is important to study the electrical transport and percolation behaviour in these superconductor-insulator composites.

The study of superconducting small aggregates, clusters and particles is very important from both fundamental and technological standpoint (1-7). Due to the granular nature of these materials with short coherence length (8) and large penetration depth (9), it is interesting to study the percolation and superconductivity of composites consisting of a superconductor embedded in an insulator medium. The percolation studies in metal-insulator composites are possible only on composite systems which are chemically non-reacting under the high processing temperature. The transport properties of normal metal insulator percolation systems have been extensively studied over the years (10). Recently there were a few studies on the percolation behaviour of
superconductor-normal metal composites based on the electrical transport and magnetisation properties (11-13). Since the resistivity ratio $\frac{\rho_s}{\rho_n}$ [where $\rho_s$ is the resistivity of the superconductor, and $\rho_n$ is the resistivity of normal metal at room temperature] is very small for the superconductor-normal metal composite system, the percolation model which describes the normal-state transport behaviour of the composite system cannot be applied strictly to such a system. A high Tc superconductor-insulator system is very difficult to obtain without compromising the superconducting properties. High Tc superconductors require prolonged heating at the processing temperature [$>850^\circ C$] for obtaining superconducting phase and most superconductor-insulator system do react chemically with each other under such annealing condition, reducing the superconducting transition temperature drastically (12). We have synthesised a few insulator materials which were found to be chemically non reacting with YBCO superconductor at the processing temperature, making percolation studies in superconductor-insulator system possible.

V.2 Percolation Model

Percolation model was originally proposed to describe the spreading of fluid through porous media, branching polymers from a gel, electron migration in a solid, disease infection in a community and other similar phenomena (14). Because of its generality and relative simplicity, this has found many applications ranging from the physics of quarks to the extraction of oil from sand stone.
Consider a regular lattice, where lattice sites can have two states either black or white (14). A cluster is defined as a group of black sites connected by nearest neighbour distances. \( V = V_c \), a critical point below which, only finite clusters exist but for \( V > V_c \), a fraction of the black sites belong to an infinite cluster and a percolation is possible. Below the percolation threshold, \( V < V_c \), there is no infinite cluster of black sites. From \( V_c \), the fraction of sites belonging to the infinite cluster grows drastically, and it has a non-analytic point at \( V_c \). This non-analytic nature is a characteristic for the percolation threshold and is usually described by a power law asymptotically close to \( V_c \).

In the case of a metal-insulator composite system, the resistivity of the latter is very high. If metal is added to an insulator, the resistivity of the composite remains more or less same as that of the insulator up to a critical volume fraction of metal in the composite. If the volume fraction of the metal increases beyond the critical volume, the resistivity reduces drastically to that of pure metal. The critical volume fraction of metal required to have a continuous network or to become an infinite cluster is called the percolation threshold value. The transport properties can be described by a set of exponential equations below and above the threshold volume (1, 14, 15).

The relations are,

\[
\rho = \rho_0 (V_m - V_c)^{\gamma} \quad \text{for} \quad V_m > V_c \tag{1}
\]

\[
\rho' = \rho'_0 (V_c - V_m)^{\gamma'} \quad \text{for} \quad V_m < V_c \tag{2}
\]

where \( \rho \) and \( \rho' \) are the resistivities of the composites, \( \rho_0 \) and \( \rho'_0 \) are constants,
The volume fraction of the metal in the system and $V_c$ the threshold volume. 't' and 'u' are critical exponents describing the transport properties. The values of $V_c$, 't' and 'u' obtained for different systems of composites vary due to many factors. The critical exponents 't' and 'u' are a measure of the order of interaction between normal metal and insulator. The value obtained for percolation threshold is around 17 vol.% of metal in the system for a perfect metal-insulator composite without any interaction or reaction between the two. The expected values of critical exponents are $t \sim 1.7$ and $u \sim 0.7$ approximately. The values obtained by experimental methods vary slightly around this value. An appreciable variation of critical exponents from the above values indicate, that the system is not forming a perfect non-reacting composite. In this Chapter we present the percolation studies on superconductor-ceramic insulators [YBCO-YBa$_2$HfO$_{3.5}$*, YBCO-GdBa$_2$HfO$_{3.5}$ and YBCO-SmBa$_2$HfO$_{3.5}$] systems based on x-ray diffraction and electrical measurements. In these superconductor-insulator composite systems the percolation model holds and the superconductivity of YBCO is retained without deteriorating under severe heat treatment.

V.3 YBa$_2$Cu$_3$O$_{7-\delta}$-YBa$_2$HfO$_{5.5}$ Percolation System

The electrical transport properties and percolation behaviour of YBa$_2$Cu$_3$O$_{7-\delta}$-YBa$_2$HfO$_{5.5}$ superconductor-insulator composite system have been

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studied in detail by the x-ray diffraction and the temperature-resistivity measurements.

V.3.1 Preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$-YBa$_2$HfO$_{5.5}$ Composites

Pure YBCO was prepared from high purity $\text{Y}_2\text{O}_3$, $\text{BaCO}_3$ and $\text{CuO}$ by solid state reaction. The compound YBa$_2$HfO$_{5.5}$ [YBHO] was also prepared by solid state reaction and the details of the processing and characterisation has already been described in Chapter IV. The YBCO-YBHO composites have been prepared by mixing different volume percentages of YBCO and YBHO taking into account their theoretical density values i.e. $6.4\text{ gm/cm}^3$ for YBCO and $7.129\text{ gm/cm}^3$ for YBHO. The samples were pressed in the form of pellets of 10 mm diameter and 2 mm thickness and sintered at temperatures in the range of $950^\circ\text{C}$ to $1350^\circ\text{C}$ for 15 h in air depending upon the volume percentage of YBHO in the composite. Table V.1 shows the different volume ratios of composites prepared from zero volume percentage to 100 volume percentage of YBHO along with their sintering temperatures. It was observed that, as the vol.% of YBHO in the composite increases the sintering temperature also increases. The samples were then cooled slowly at the rate of $2^\circ\text{C/min}$ to room temperature in air. For YBCO-YBHO composites containing upto 70 vol.% of YBHO the sintering temperature was $< 1020^\circ\text{C}$ and for composites containing YBHO $> 70$ vol.% , the sintering temperature had to be increased above $1020^\circ\text{C}$ in order to get good quality sintered samples. The sintered densities of the composite samples were measured by conventional
X-ray Diffraction Studies on \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} - \text{YBa}_2\text{HfO}_{5.5} \) Composites

X-ray diffraction studies were carried out to identify different phases existing in YBCO-YBHO composite and to see the extent of reactions between the two compounds. The XRD patterns of YBCO-YBHO composites for 0 to 100 vol.% of YBHO in the system are given in Fig. V.1. In the XRD patterns of the composites up to 70 vol.% of YBHO, two distinct sets of peaks, one corresponding to YBCO having an orthorhombic structure,
Fig V.1 X-ray powder diffraction pattern for different vol % of YBa$_2$HfO$_{3.3}$ in the YBa$_2$Cu$_3$O$_{7.8}$-YBa$_2$HfO$_{3.3}$ composites (A) 0% (B) 10% (C) 30% (D) 50% (E) 70% and (F) 100%
and the other corresponding to YBHO, are clearly visible. There is no evidence of any additional peaks other than those of YBCO and YBHO in the XRD patterns indicating that, there is no detectable reaction [within the precision of XRD] between the two compounds even after severe heat treatment upto 1020°C. At this elevated temperature normally one expects decomposition of YBCO along with some reaction. But in the composite system, the rate of decomposition is reduced due to the presence of YBHO and the orthorhombic structure and superconducting properties of YBCO were retained. For the composites with YBHO > 80 vol.%, the sintering temperature was above the peritectic temperature of YBCO (~1030°C) and therefore the formation of 211 (Y₂BaCuO₅) phase with YBCO is expected, but in the present study the XRD patterns did not show the presence of 211 phase in the system. In the case of almost all known ceramic insulators, the superconducting properties of YBCO and its orthorhombic structure is lost, when it is processed along with the insulator above 950°C. But in the case of YBCO-YBHO the structure and superconducting properties of YBCO are not affected even after a severe heat treatment above 1000°C for a prolonged period.

V.3.3 Temperature-Resistivity Measurements on YBa₂Cu₃O₇₋₆-YBa₂HfO₅.₅ Composites

The resistivities of the YBCO-YBHO composites with different volume percentages of YBHO were measured by four-probe method in the temperature range 300-77K. The temperature dependence of normalised resistivities [$\frac{\rho}{\rho_r}$]
with different volume percentages of YBHO is shown in Fig. V.2. Composites upto 70 vol.% of YBHO showed metallic behaviour and gave a zero resistivity superconducting transition temperature above 90K. Even though there is superconducting transition for 80 vol.% of YBHO in the composite, its resistivity does not become zero upto a temperature of 77K. This can be due to the absence of a superconducting network through the matrix of the composite because of low volume percentage of YBCO in the composite. Samples with higher vol.% of insulator [vol.% of YBHO > 80] exhibited high value of resistance in the normal temperature and a two probe method was used to measure their resistivity. The resistivity was found to be of the order of $10^{11} \Omega \text{cm}$. The superconducting percolation threshold for YBCO-YBHO composites lies around 20 vol.% of YBCO in the composite. This means that, when the volume percentage of YBCO is $\sim 20$ or above, there are interconnected networks of superconducting grains for the supercurrent to pass through the composite material. But for lower volume percentage of YBCO [$< 20$], the continuous network of superconducting grains breaks away and the resistance become nearly equal to that of pure insulator YBHO.

The electrical transport properties of the composite in the normal state are studied in detail. The variation of normal state resistivity for different vol.% of YBHO in the composite are plotted in Fig. V.3. The resistivity '$\rho$' and temperature coefficient of resistivity $\alpha = \left[ -\frac{1}{\rho} \frac{d\rho}{dt} \right]$ at room temperature are also plotted as a function of vol.% of YBCO [Vs] in the composite. In the normal state, YBCO is a metallic conductor with
Fig V.2 Variation of normalized resistivity $\rho/\rho_i$ with temperature for different vol % of $\text{YBa}_2\text{HfO}_{3.5}$ in the $\text{YBa}_2\text{Cu}_3\text{O}_{7.5}-\text{YBa}_2\text{HfO}_{3.5}$ composites (A) 0% (B) 10% (C) 30% (D) 50% (E) 70% and (F) 80%
Fig V.3  (A) Variation of normal state resistivity $\rho$ and (B) temperature coefficient of resistivity $\alpha=(1/\rho) (d\rho/dt)$, at room temperature for different vol% Vs for YBa$_2$Cu$_3$O$_{7-\delta}$. 

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resistivity $\sim 1$ m $\Omega$ cm, which is nearly 12 orders of magnitude lower than that of YBHO. The normal state resistivity of YBCO-YBHO composite samples is dominated by YBCO with a significant drop of $\rho$ occurring near $Vs \sim 20$ vol.%. The behaviour of $\rho$ correlates with that of $\alpha$ which increases sharply towards that of YBCO starting from $Vs \sim 20$ vol.%. Therefore the percolation threshold value 'Vc' for the normal state transport properties of the composite is $\sim 20$ vol.% of YBCO. Thus the superconducting percolation threshold and the normal state percolation threshold values of YBCO-YBHO composites lie in the same range.

The normal state transport properties of ceramic insulator-superconductor system can be described by a set of equations (15-16),

$$\rho = \rho_0 (Vs - Vc)^t \text{ for } Vs > Vc \quad \text{........... [3]}$$

$$\rho' = \rho'_0 (Vc - Vs)^u \text{ for } Vc > Vs \quad \text{........... [4]}$$

where $\rho_0$ and $\rho'_0$ are constants, Vc is the critical volume fraction at which transport properties change drastically and it is called the percolation threshold. $Vs$ is the vol.% of YBCO in the composite and 't' and 'u' are the critical exponents describing the transport properties of the composite system. The values of $\rho_0$, $\rho'_0$, 't' and 'u' are found from a log-log plot of $\rho$ versus $(Vs - Vc)$ and $\rho'$ versus $(Vc - Vs)$. For an idealized insulator-conductor system $Vc \sim 17\%$, $t = 1.7$ and $u = 0.7$. The values of $Vc$ are taken such that a log-log plot of equations (3) and (4) gives a straight line. Figures V.4(A) and (B) show
Fig V.4 (A) Log-log plot of resistivity $\rho$ vs $(V_s - V_c)$; where $V_s$ is the vol% of YBa$_2$Cu$_3$O$_{7-\delta}$ in the YBCO-YBHO composite and $V_c$ is the percolation threshold value.
Fig V.4 (B) Log-log plot of resistivity $\rho'$ vs $(V_c-V_s)$ where $V_s$ is the vol% of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in the YBCO-YBHO composite and $V_c$ is the percolation threshold value.
the log-log plots of $\rho$ versus $(V_s - V_c)$ and $\rho'$ versus $(V_c - V_s)$ respectively. The least-square fits were performed to determine the slope of the plots which gave the exponents 't' and 'u' as 1.7 and 0.65 respectively with a percolation threshold $V_c = 0.23$ and the values for $\rho_0$ and $\rho'_0$ calculated as $4.23 \, \text{m} \, \Omega \, \text{cm}$ and $8.9 \times 10^{-11} \, \text{m} \, \Omega \, \text{cm}$ respectively. The values of critical exponents obtained for YBCO-YBHO composites agree reasonably well with the theoretical values for an idealized metal-insulator percolation system.

V.4 YBa$_2$Cu$_3$O$_{7.8}$ -GdBa$_2$HfO$_{5.5}$ Percolation System

The electrical transport properties and percolation behaviour of YBa$_2$Cu$_3$O$_{7.8}$ -GdBa$_2$HfO$_{5.5}$ superconductor-insulator composites have been studied by the x-ray diffraction and the temperature-resistivity measurements.

V.4.1 Preparation of YBa$_2$Cu$_3$O$_{7.8}$ -GdBa$_2$HfO$_{5.5}$ Composites

The phase pure YBCO and the single phase GdBa$_2$HfO$_{5.5}$ [GBHO] were prepared from their constituent high purity oxides as described in Chapter IV. The YBCO-GBHO composites were prepared by mixing them thoroughly with different volume percentages of GBHO taking into account their theoretical densities, i.e. $6.4 \, \text{gms/cm}^3$ for YBCO and $7.9 \, \text{gm/cm}^3$ for GBHO. The mixture was then pelletised and sintered following the similar procedure as described in the case of YBCO-YBHO composite. The sintering temperature varies from $950^\circ \text{C}$ to $1350^\circ \text{C}$ depending upon the volume percentage of GBHO in the composites. Table V.2 gives the different volume ratios of composites
prepared from 0 to 100 vol.% of GBHO along with their sintering temperatures. As the vol.% of GBHO increases, the sintering temperature was also found to increase.

<table>
<thead>
<tr>
<th>Vol. % of YBCO</th>
<th>Vol % of GBHO</th>
<th>Sintering temp. (°C)</th>
<th>Density (gm cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>950</td>
<td>6.12</td>
</tr>
<tr>
<td>95</td>
<td>5</td>
<td>955</td>
<td>6.28</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>960</td>
<td>6.24</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>970</td>
<td>6.18</td>
</tr>
<tr>
<td>70</td>
<td>30</td>
<td>980</td>
<td>6.13</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>1000</td>
<td>6.15</td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>1020</td>
<td>6.16</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>1030</td>
<td>6.18</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>1040</td>
<td>6.18</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>1350</td>
<td>6.13</td>
</tr>
</tbody>
</table>

The rate of cooling of these composite samples [2°C/min] was similar as in the case of YBCO-YBHO composites. For YBCO-GBHO composites containing up to 70 vol.% of GBHO the sintering temperature was < 1020°C and that of GBHO > 70 vol.%, the sintering temperature had to be increased above 1020°C in order to get well sintered samples. The sintered densities of the samples measured by Archimedes method are also given in Table V.2.
V.4.2 X-ray Diffraction Studies on YBa$_2$Cu$_3$O$_{7.5}$-GdBa$_2$HfO$_{5.5}$ Composites

Powder X-ray diffraction studies were carried out on YBCO-GBHO composites to monitor the reaction between the two compounds. Figure V.5 shows the XRD patterns taken on different volume ratios of the composites. Upto 70 vol.% of GBHO, two distinct sets of peaks, one corresponding to YBCO having an orthorhombic structure, and the other to GBHO are clearly visible in the XRD patterns. No additional peaks other than YBCO and GBHO were observed in the XRD patterns, indicating that, there is no reaction between the two compounds even after severe heat treatment upto 1020°C. No decomposition of YBCO was observed at this elevated temperature which may be due to the presence of the second phase GBHO in the composites. For the composites with GBHO > 70 vol.%, the sintering temperature was above the peritectic temperature of YBCO [~1030°C] and there was no evidence of green phase [Y$_2$BaCuO$_3$] or any other impurity phases in the system.

V.4.3 Temperature-Resistivity Measurements on YBa$_2$Cu$_3$O$_{7.5}$-GdBa$_2$HfO$_{5.5}$ Composites

The temperature-resistivity measurements were done by dc four-probe method as described in Chapter II. Figure V.6 shows the temperature-resistivity curves for different volume percentage of GBHO in the composite in which the normalised resistivity $\frac{\rho}{\rho_f}$ is plotted against temperature. All the composites upto 70 vol.% of GBHO showed a metallic behaviour in their
Fig V.5  X-ray powder diffraction pattern for different vol% of GdBa,HfO$_{5.5}$ in the YBa$_2$Cu$_{3.8}$-GdBa$_2$HfO$_{5.5}$ composites (A) 0% (B) 10% (C) 30% (D) 50% (E) 70% and (F) 100%
Fig V.6 Variation of normalized resistivity $\rho/\rho_o$ with temperature for different vol\% of GdBa$_2$HfO$_{5.5}$ in the YBa$_2$Cu$_3$O$_{7.5}$-GdBa$_2$HfO$_{5.5}$ composites (A) 0\% (B) 10\% (C) 30\% (D) 50\% (E) 70\% and (F) 80\%
resistivity curves and gave a superconducting transition temperature of above 90K. Even though there is a superconducting transition for 80 vol.% of GBHO in the composite, its resistivity does not become zero up to a temperature of 77K. This may be due to the lack of sufficient superconducting networks through the matrix of the composites because of the low vol.% of YBCO. For still higher volume percentages of GBHO, its normal state resistivity becomes too high and four-probe method could not be used to measure the resistivity. The resistivity of these samples were measured by a Keithley solid state electrometer using two-probe method and was found to be of the order of $10^{-11} \Omega \text{cm}$. The superconducting percolation threshold for YBCO-GBHO composites lies around 20 vol.% of YBCO in the composite.

The variation of normal state resistivity at room temperature for different volume percentages of GBHO is plotted in Fig. V.7 along with the temperature coefficient of resistivity [$\alpha$]. Both the normal state resistivity and temperature coefficient of resistivity showed a sharp deviation in their values at about 80 vol.% of GBHO in the composite. Thus the normal state percolation threshold value for the YBCO-GBHO composite lies around 20 vol.% of YBCO. The actual value of the percolation threshold volume can be calculated from the equations governing the transport properties of the composites [equations 3 and 4] by considering GBHO as an insulator and YBCO at room temperature as metal. The percolation threshold value $V_c$ is taken such that the log-log plot gives a straight line. The log-log plot of equation [3] and [4] for YBCO-GBHO composites are shown in Fig. V.8 [A & B].
Fig V.7 (A) Variation of normal state resistivity $\rho$ and (B) temperature coefficient of resistivity $\alpha = (1/\rho) \left( \frac{dp}{dt} \right)$ at room temperature for different vol% Vs for YBa$_2$Cu$_3$O$_{7-\delta}$.
$V_c = 0.22, \ t = 1.66, \ \rho_o = 4.568 \ \text{mΩ cm.}$

Fig V.8 (A) Log-log plot of resistivity $\rho$ vs $(V_s-V_c)$ where $V_s$ is the vol% of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in the YBCO-GBHO composite and $V_c$ is the percolation threshold value.
Fig V.8 (B) Log-log plot of resistivity $\rho'$ vs $\text{Vc-Vs}$ where Vs is the vol% of $\text{YBa}_2\text{Cu}_3\text{O}_{\gamma/4}$ in the YBCO-GBHO composite and Vc is the percolation threshold value.
values of $\rho_0$, $\rho_0'$, $t$ and $u$ are calculated from the log-log plot of $\rho$ versus $(V_s-Vc)$ and $\rho_0'$ versus $(Vc-Vs)$ respectively. The exponents 't' and 'u' are found to be 1.66 and 0.625 respectively with a percolation threshold $Vc = 0.22$. The values of $\rho_0$ and $\rho_0'$ are calculated to be $4.568 \ \text{m} \ \Omega \ \text{cm}$ and $1.15 \times 10^{12} \ \text{m} \ \Omega \ \text{cm}$ respectively.

The percolation threshold value $Vc$ is nearly equal to that for an ideal insulator-conductor composite system. The values of critical exponents 't' and 'u' agrees well with those values expected theoretically. Thus the percolation model for the normal state transport properties show that, YBCO-GBH0 forms a real composite without any detrimental reaction or interaction between the two. Processing temperature for composites with higher volume percentages of GBH0 was much higher than that of pure YBCO. At this elevated temperature there are chances for decomposition of YBCO and also for reaction with GBH0. But the percolation studies show that the system forms a composite without any decomposition of YBCO or any reaction between the two compounds. Hence it is clearly established that a substantial addition of GBH0 in YBCO will not affect the transport properties at normal temperatures.

V.5 $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} - \text{SmBa}_2\text{HfO}_{5.5}$ Percolation System

The percolation behaviour of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} - \text{SmBa}_2\text{HfO}_{5.5}$ (YBCO-SBHO) system have also been studied. The electrical transport and percolation behaviour of YBCO-SBHO composite were found to be similar to those of
YBCO-YBHO and YBCO-GBHO composite systems. Hence we include only the results obtained for YBCO-SBHO system. YBCO-SBHO system showed a superconducting percolation threshold volume of 20 with normal state percolation volume ~20%. The values of $\rho_0$, $\rho_0'$, $t$ and $u$ were calculated from the log-log plot of $\rho$ versus $(V_s-V_c)$ and $\rho'$ versus $(V_c-V_s)$ and are $V_c = 0.22$, $t = 1.64$, $u = 0.6$, $\rho_0 = 4.657$ m$\Omega$cm and $\rho_0' = 1.568 \times 10^{12}$ m$\Omega$cm.

The percolation studies on YBCO-SBHO system also showed that this system forms a composite without any decomposition of YBCO or any reaction between the two compounds. Hence the addition of SBHO in YBCO also does not affect the transport properties.

V.6 Percolation Study in YBa$_2$Cu$_3$O$_{7-\delta}$ - YBa$_2$HfO$_{5.5}$ Rapidly Quenched Samples

In addition to slow cooled YBa$_2$Cu$_3$O$_{7-\delta}$ - YBa$_2$HfO$_{5.5}$ samples, we found that percolation is possible in the case of rapidly quenched YBCO-YBHO composites. The chemical reactivity and high temperature superconductivity in YBCO-YBHO composites by rapid quenching in air have been studied by XRD and resistivity measurements*. It was found that the common procedure of slow cooling at the rate of 2°C/min or annealing for several hours at temperatures between 700-500°C after high temperature sintering is not essential to obtain superconductivity in YBCO-YBHO composites. No

detectable chemical reaction between YBCO and the non metal YBHO was observed even under severe heat treatment followed by rapid quenching in air. A superconducting transition of 92K was obtained in this system for a wide composition range by directly quenching these samples in air from a sintering temperature of 950°C.

We have carried out a detailed study on the percolation behaviour of YBCO-YBHO system after quenching rapidly in air in addition to the normal processing of slow cooling. It is interesting to note that even in the rapidly quenched YBCO-YBHO composite systems the percolation model agrees very well with that of the slow cooled samples. YBCO-YBHO composites rapidly quenched in air showed a percolation threshold volume of 20% with normal state percolation volume \( \approx 23\% \). The values of \( p_0, p_0', t, u \) were calculated from the log-log plot of \( \rho \) versus \( (V_s-V_c) \) and \( \rho' \) versus \( (V_c-V_s) \) and are found to be 4.44 m\( \Omega \)cm, 1.36 \( \times 10^{12} \) m\( \Omega \)cm, 1.68 and 0.67 respectively. The values agree well with the theoretically predicted values for an idealized conductor-insulator system.

V.7 Discussions

The results obtained from the XRD and resistivity measurements on the percolating systems, YBCO-YBHO, YBCO-GBHO and YBCO-SBHO show that the superconductor and insulators remain as two separate phases in the composites with their own characteristics even under severe heat treatments. Table V.3 gives a comparative study of the percolation threshold.
volumes in superconducting and normal states, critical exponents 't' and 'u' for all the three systems. The superconducting and normal state percolation threshold values of these composites were found to be in the same range (about 20 vol.% of YBCO). The critical exponent 't' which describes the transport properties in the metallic side of the composite system agrees with that expected for an idealized conductor-insulator system.

Table V.3 Comparison of critical parameters of YBa$_2$Cu$_3$O$_{7-\delta}$-REBa$_2$HfO$_{5.5}$ composite percolation systems

<table>
<thead>
<tr>
<th>System</th>
<th>Percolation threshold vol.%</th>
<th>t</th>
<th>u</th>
<th>$\rho_0$</th>
<th>$\rho_0'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>YBCO-YBHO</td>
<td>~20</td>
<td>23</td>
<td>1.70</td>
<td>0.65</td>
<td>4.23</td>
</tr>
<tr>
<td>YBCO-GBHO</td>
<td>~20</td>
<td>22</td>
<td>1.66</td>
<td>0.625</td>
<td>4.568</td>
</tr>
<tr>
<td>YBCO-SBHO</td>
<td>~20</td>
<td>22</td>
<td>1.64</td>
<td>0.60</td>
<td>4.657</td>
</tr>
<tr>
<td>YBCO-YBHO (Rapidly quenched)</td>
<td>~20</td>
<td>23</td>
<td>1.68</td>
<td>0.67</td>
<td>4.44</td>
</tr>
</tbody>
</table>

This indicates that the systems form good composites up to 80 vol.% for YBHO, GBHO and SBHO samples. The values obtained for the critical exponent 'u' which describe the transport properties in the insulating side of the composites are also found to be well matched with that of an idealized conductor-insulator system. This observation implies that there is no reaction between YBCO and the ceramic insulators YBHO, GBHO or SBHO even at 1030°C or above.
The XRD measurements show that the orthorhombic structure of superconducting YBCO has not been affected at all, by the addition of the insulators even at the processing temperatures. No evidence of the decomposition of the superconducting phases or any additional phases other than those of YBCO and insulators were observed in the XRD patterns. The observations of high temperature superconductivity with a transition temperature above 90K in all the three composite systems having ~70 vol.% of insulating material in the composite, may be of fundamental importance in view of very short coherence length \([\sim 10 \text{ Å}]\) of YBCO superconductors.

It may be noted that percolation is possible even in the case of rapidly quenched YBCO-YBHO composites without any deterioration in the superconducting properties of YBCO. But we could not observe superconductivity in rapidly quenched YBCO-GBHO and YBCO-SBHO composite systems and hence no percolation measurements were possible in these system.

The chemical non-reactivity between YBCO and insulator ceramic materials YBHO, GBHO and SBHO even under severe heat treatment (\(> 950^\circ\text{C}\)) makes these insulators as idealized substrate material for YBCO thick and thin films. The percolation studies carried out on these composites confirmed their suitability as substrates for YBCO films. In the proceeding Chapters we have concentrated on the fabrication of YBCO thick films on these non-reacting substrates.
References


