Chapter 6

Studies on the pinning energy of RE substituted (Bi,Pb)-2212 superconductors

Take time to deliberate, but when the time for action has arrived, stop thinking and go in.
— Napoleon Bonaparte, 1769–1821.

6.1 Introduction

A very important parameter of a type-II superconductor is the critical current density \( J_c \) at which the Abrikosov vortices depin and start to move under the influence of the Lorentz force. The vortex drift induces an electric field \( E \) which causes a voltage drop along the superconductor. Consequently, at current densities \( J > J_c \) energy is dissipated and the resistivity \( \rho = E/J \) becomes finite. In high \( T_c \) superconductors (HTSs) thermally activated depinning of flux lines causes energy losses even at \( J < J_c \). HTSs are, therefore, better char-
acterized by their nonlinear current-voltage law $E = E(J)$, which defines $J_c$ as the current density at which $E(J)$ deviates noticeably from zero and starts to rise steeply, according to a power law $E = E_c(J_c/J)^n$ with $n \gg 1$ which reflects the abruptness of the transition and determines the suitability of the superconductor for technological applications and $E_c$ is the standard criterion of $1 \mu V/cm$ [1-4]. The finite $E$ at $J < J_c$ leads to the decay of persistent currents and to a decrease of magnetic moment which causes flux creep. The sharpness of the $E$-$J$ characteristics is governed by the microstructural homogeneity, flux-creep [5] and/or the vortex glass-liquid transition [6] of the superconductor.

A high $n$-value is associated with good homogeneity. The dependence of the $n$-value on the magnetic field is related to the quality of a superconductor. The resistive transition index is observed to fall with the increase in magnetic field. The steeper the negative slope, the more dominant is the role of the microstructure. Together with the critical current density ($J_c$), the $n$-value is important in applications such as persistent-mode NMR magnets [7] for extrapolating to the low operating electric fields, and cable-in-conduit-conductor fusion magnets for calculating operating margins and interpreting data for prototype systems [8-10]. The origin of the $n$-value in high-temperature superconducting wires is generally attributed to distributions in the critical current [11-16] arising from distributions in the elementary flux-pinning forces (intrinsic effects) [11,12] and from nonuniformities in the cross-sectional area of the superconducting filaments (extrinsic effects) [14-16]. Thus the $n$-value is being commonly used as a quantitative figure of merit or ‘quality index’ [4]. Hence, the $E$-$J$ characteristics are closely related to the intrinsic properties. This complex mechanism of dissipation in HTSs is a matter of interest because of their technological significance and a detailed analysis of $E$-$J$ characteristics is essential for a better understanding of the relationship between the microstructure and current carrying properties of polycrystalline superconductors rather than single crystals for practical applications. In this chapter, a detailed analysis of the $E$-$J$ characteristics and the associated $n$-indices of RE-free and
RE substituted (Bi,Pb)-2212 superconductor at different magnetic fields are discussed and an assessment of the suitability of the material for application in persistent mode magnets is performed.

6.2 Experimental details

Samples with the nominal stoichiometry of Bi$_{1.6}$Pb$_{0.5}$Sr$_{2-x}$RE$_x$Ca$_{1.1}$Cu$_{2.1}$O$_{8+y}$ ($0 \leq x \leq 0.5$ and RE = Gd, Tb, Dy and Ho) were prepared by solid-state synthesis using high purity oxides and carbonates, namely Bi$_2$O$_3$, PbO, SrCO$_3$, CaCO$_3$, CuO and Tb$_4$O$_7$ (Aldrich, > 99.9 %). The ingredients were accurately weighed using an electronic balance and thoroughly homogenized using a planetary ball-mill with agate bowl and balls in acetone medium for 2 hours. The homogeneous mixtures, thus obtained were calcined in three stages in air at 800°C for 15 h + 815°C for 40 h + 830°C for 40 h. Intermediate grinding in acetone medium was done between each stage of calcination to improve the homogeneity of samples. The samples were then pelletized under a pressure of 500 MPa. The pellets were heat-treated for 120 h with a schedule of 845°C for 60 h + 848°C for 60 h employing an intermediate pressing under the same pressure. In order to confirm the phase formation and superconductivity, the structural and superconducting characterisations were performed as mentioned in the previous chapters. The samples are hereafter denoted as RE$_x$, where RE is the rare earth used and $x$ represents the last digits of the RE stoichiometry. For example, Tb150 and H150 denote the Tb and Ho substituted samples with the stoichiometry, $x = 0.150$. Similarly, G0, Dy0, Tb000 and H000 represent RE-free samples.

Current and potential leads of high-grade copper wires were soldered to the samples with silver coating. Cylindrical pellets were shaped into rectangular form with the dimensions 12×4×1 mm$^3$ on which the potential leads, separated by a distance of 5 mm were placed at the central part of the specimen.
The transport \( J_c \) in the self-field and E-J characteristics of the samples under zero and fixed fields namely, 0.32 T and 0.64 T, were measured at 64 K by four-probe method in a liquid \( \text{N}_2 \) bath cryostat with provision for vacuum. The direction of current was parallel to the direction of the pressed surface and magnetic field was applied perpendicular to the pressed surface of the pellet. A computer controlled dc-pulse method with four-probe arrangement was used to determine E-J characteristics using a constant current source (Aplab 9711P) and subsequently to determine the transport \( I_c \) of the samples. The pulse method effectively minimize the Joule heating from current leads and contacts by providing sufficient cooling time between each pulse. Thus it also avoids the influence of the ramp-rate on E-J characteristics. Transport critical current (\( I_c \)) values were determined using the four-probe method with a standard criterion of 1\( \mu \text{V/cm} \), derived from the resistance between voltage terminals. The \( J_c \) values of the pure and RE substituted (Bi,Pb)-2212 samples were calculated from \( I_c \) and the total cross-sectional area of the samples.

### 6.3 Transport E-J characteristics

From the structural analysis of the samples, it is clear that substituted RE atoms have successfully entered in the crystal structure of (Bi,Pb)-2212 system. The substitution of a trivalent/tetravalent RE atom in the crystal structure of (Bi,Pb)-2212 controls the hole concentration of the \( \text{CuO}_2 \) layers as a whole. This controlling mechanism of holes in the \( \text{CuO}_2 \) planes is discussed in chapter 4, i.e., when trivalent/tetravalent RE atoms are substituted into the (Bi,Pb)-2212 system, each RE atom supply additional electrons to the system which fills the holes present in the crystal. Hence, the hole concentration in the \( \text{CuO}_2 \) plane decreases and the system reaches an optimal doped state with an increased \( T_c \). The variation of \( T_c \) with RE concentration is given in table 4.1 in chapter 4. The results show that the RE substituted (Bi,Pb)-2212 samples have
much higher $T_c$ values at optimum concentrations compared to the RE-free sample.

The RE-free and RE substituted (Bi,Pb)-2212 samples are further analysed from the E-J characteristics using one-dimensional flux-creep model, wherein the flux-creep is caused by a thermally activated motion of flux-lines in superconductors. This motion is characterized by a velocity, strongly dependent on the local current density. Maxwell's equation of the form,

$$\left( \frac{\partial B}{\partial t} \right) = -\left( \frac{\partial E}{\partial x} \right)$$

(6.1)

is used to understand the flux motion in the presence of applied magnetic field where, $E$ is the local electric field which can be related to the flux density and the velocity of the thermally-activated flux motion $v$ by the relation, $E = vB$. The velocity of the vortex motion in a thermally activated process is given by

$$v = v_{c} e^{-[U(J)/k_{B}T]}$$

(6.2)

where $U(J)$ is the pinning barrier potential and $v_{c}$ is the velocity when $U(J) = 0$, $U_{c}$ is the pinning energy. In the case that the pinning energy has a logarithmic dependence on the current,

$$U(J) = U_{c} ln \left( \frac{J_{c}}{J} \right)$$

(6.3)

and it follows that the electric field equals [17]

$$E = E_{c} \left( \frac{J_{c}}{J} \right)^{n}$$

(6.4)

Figures 6.1-6.4 show the E-J characteristics (log $E - \log J$ curves) of the RE-free and RE (Gd, Dy, Tb and Ho) substituted (Bi,Pb)-2212 samples measured at 0.0, 0.32 and 0.64 T at 64 K. The important inference is that the self-field
Figure 6.1: E-J characteristics of Gd substituted (Bi,Pb)-2212 superconductors at 0.32 and 0.64 T compared with Gd-free sample.

\[ J_c \] of all the RE substituted samples are higher than the pure sample. The self-field \( J_c \) attains a peak value after a systematic increase as the RE content increases. The observed peak value of self-field \( J_c \) is higher than the RE-free sample. Almost a linear behaviour is seen in the E-J characteristics measured at 0.0, 0.32 and 0.64 T which is due to the thermally activated flux-flow. All the E-J characteristics fit well with the equation \( \log E = n \ln J + C \), where \( C \) is a constant and the slopes of these curves give the n-index, which has been tabulated in table 6.1. It is found that, both in self- and in-fields, the maximum value of n-index is obtained at the same \( x \) value for each RE where their best properties were obtained (Gd, Dy, Tb and Ho substituted samples show best properties at \( x = 0.2, 0.2, 0.075 \) and \( 0.075 \), respectively) and hence a maximum current flow with minimum dissipation of energy. At self-fields all the samples show relatively high n-index while at in-fields, it decreases (Table 6.1), since the n-index is a field dependent parameter. The Gd and
Figure 6.2: E-J characteristics of Dy substituted (Bi,Pb)-2212 superconductors at 0.32 and 0.64 T compared with Dy-free sample.

Figure 6.3: E-J characteristics of Tb substituted (Bi,Pb)-2212 superconductors at 0.32 and 0.64 T compared with Tb-free sample.
Tb/Ho substituted samples have better n-index \((n>15)\) at 0.0 T and 0.32 T for \(x\) values 0.2 and \((0.050 \leq x \leq 0.125)\), respectively. However, in contrast to Gd and Dy substituted samples, Tb and Ho substituted samples have an n-index greater than 15 even at an applied field of 0.64 T at 64 K for \(x\) values \((0.075 \leq x \leq 0.125)\) and \((0.050 \leq x \leq 0.125)\) respectively. The Dy substituted samples show the best self-field performance, but has a comparatively poor in-field performance. The observations reveal that at self-field and applied-fields (0.32 T and 0.64 T), the flux-lines are in glass-state (weak creep) for samples with \(n>15\) and those in all the remaining samples with \(n<15\) are in liquid-state (strong creep) [18].

The decay of persistent current in a superconducting magnet is found to be closely related to the n-index of the superconductor. In the case of an NMR magnet, the decay of the magnetic field and hence, the decay of the persistent
current should be smaller than $10^{-2}$ ppm/h. For an n-index $\sim 20$, the magnitude of the persistent current is calculated to be only 36% of $J_c$ and a high value of persistent current density of 55% $J_c$ is obtained for an n-index of $\sim 34$ for the Bi-2212 insert magnet of the high-field NMR magnet system [17]. Thus, the RE substituted (Bi,Pb)-2212 samples with an n$>20$ at applied fields, under transport current flow, can be used for magnetic applications such as insert-magnets. A correlation between n-value (or $U_c$) and $J_c$ for different samples is observed by comparing the $U_c$-curves (Figures 6.5(a)–6.5(d)) with the $J_c$ values (Table 6.1), i.e., high $J_c$ values are generally found for samples with large n-values (n$>15$), while small $J_c$ values (x$<0.05$) are typically observed for samples with low n-values (n$<15$). Thus, the general trend in the observed dissipation is that the flux-creeping effects in RE substituted (Bi,Pb)-2212 samples are weaker for the samples with larger n-indices and vice-versa. In the present work, the observed high n-indices in RE substituted (Bi,Pb)-2212 samples are at a temperature as high as 64 K and hence, there is a great scope for further drastic increase in n-indices at 4.2 K.

Figures 6.5(a)–6.5(d) show the variation of $U_c$ as estimated from the n-index with respect to x. It reveals that REs, [Tb and Ho] and [Gd and Dy], when substituted with x=0.075 and x=0.200, respectively, show the best flux pinning capability as evident from a peaking of $U_c$, both for self-field and in-fields namely, 0.32 T and 0.64 T. The relative performance of RE substituted samples in self- and in-fields is evaluated by comparing its $U_c$ values with those of the RE-free sample and the $U_c$ values are given in table 6.1. The RE-free sample shows $U_c$ values of 29.0 $\pm$ 0.1 meV in the self-field ($\sim 4, 10, 7$ and $6$ times lesser than best sample of Gd, Dy, Tb and Ho, respectively.) and 18.4 $\pm$ 0.1 meV and 6.6 $\pm$ 0.1 meV at 0.32 and 0.64 T (which is also lesser than best sample Gd, Dy, Tb and Ho substituted samples), respectively. It is also observed that all the RE substituted samples have better $U_c$ compared to the RE-free sample. Hence, it is concluded that the RE substituted samples have much better flux pinning properties than the RE-free sample.
Figure 6.5: Dependence of characteristic pinning energy ($U_c$) on RE concentration at self- and in-fields (0.32 T and 0.64 T).

The estimated values of activation barrier of vortex motion $U(J)$ in self- and in-fields are determined and are shown in figures 6.6–6.9 which show a logarithmic dependence on the current density over a wide range. The results show that deterioration of $U(J)$ due to the magnetic field is significantly reduced as a result of RE substitutions. This shows that doping of RE atoms at the Sr-site enhances the flux pinning properties of (Bi,Pb)-2212 superconductor. The activation potential required for the motion of fluxons is higher for RE substituted samples with higher $J_c$ and $U_c$ (or n-values), while the least is observed for the RE-free under the transport supercurrent flow. From the figure 6.6–6.9 results, it is clear that the REs, [Tb and Ho] and [Gd and Dy], when substituted with $x=0.075$ and $x=0.200$, respectively, sample has the best flux pinning strength. On extrapolating the curve to a point $U(J)=0$, the $J_c$ (at 64 K) at self- and applied fields can be found out. From the relation, $U(J) = U_c \ln \left( \frac{J_c}{J} \right)$, it is
seen that when current density (J) becomes (1/e) times $J_c$ (denoted as $J_g$) then $U_c = U(J_g)$, where $J_g$ is the current density for the transition from vortex-glass to vortex-liquid state. The value of $J_g$ determines the onset of the solid vortex-
Figure 6.7: Variation of flux-creep activation barrier $U(J)$ of Dy-free and Dy substituted (Bi,Pb)-2212 superconductors in self and applied fields.

glass to liquid transition, i.e., the vortices are in the solid-glass state for $J<J_g$ and it starts to melt to vortex-liquid state for $J>J_g$. This clearly reveals that RE substituted (Bi,Pb)-2212 superconductors exist in a solid-glass state at a much
Figure 6.8: Variation of flux-creep activation barrier $U(J)$ of Tb-free and Tb substituted (Bi,Pb)-2212 superconductors in self and applied fields.

higher current density in self- and applied-fields as compared with RE-free samples. This is another evidence for the strong pinning effect of vortices in the RE substituted (Bi,Pb)-2212 samples.
Figure 6.9: Variation of flux-creep activation barrier $U(J)$ of Ho-free and Ho substituted (Bi,Pb)-2212 superconductors in self and applied fields.

The origin of the n-value is generally attributed to the distribution in the elementary flux-pinning centers (intrinsic effects) and from the non-uniformities in the cross-sectional area of the superconductor (extrinsic effects). Here, for
samples with n>15, the intrinsic effects dominate and hence high n-values are observed [11, 12] leading to higher self-and in-field Jcs. This reveals that these samples have good flux-pinning capabilities and homogeneity and are the potential candidates for magnetic applications. At higher RE concentrations, the n-index decreases due to the domination of extrinsic effects such as the non-uniformities in the microstructure of (Bi,Pb)-2212 (weak-links). Thus, the re-
duction of n-index and hence, $J_c$ is primarily due to collective effect of the total resistance of the network of weak-links, distributed throughout the sample.

Doping of Pb at Bi-site of Bi-2212 decreases the electromagnetic anisotropy ($\gamma$) and enhances c-axis conductivity ($\sigma_c$) which slightly improves the Josephson coupling strength between the CuO$_2$ layers across the charge reservoir layer (Bi-O) which results in slight improvement in $J_c$. At sufficiently low temperatures ($T < T_c$) and magnetic fields ($H < H_{irr}$), the flux lines form 3D vortices in (Bi,Pb)-2212 superconductor. As the temperature and field increases, these 3D flux line vortices undergo a change-over to 2D pancake vortices which are mainly confined in CuO$_2$ layers. Thus, the control over the hole concentration in CuO$_2$ layer is very essential and this is achieved by RE substitution at the Sr-site of (Bi,Pb)-2212. The controlling mechanism of holes in the CuO$_2$ planes is described in chapter 4. The origin of the enhanced n-values (or $U_c$) is generally attributed to the intrinsic effects, namely, the distribution in the elementary flux pinning forces ($f_p = j_c \times B$). The main reason for the enhanced flux pinning and the high in-field performance of RE substituted (Bi,Pb)-2212 superconductor is attributed to the crystal defects created by Pb and RE atoms in the Bi and Sr-layers, respectively. Hence, at higher temperatures in presence of external field, the 2D vortices confined in the CuO$_2$ layer are strongly coupled due to Pb doping in Bi-layer, and is effectively pinned by the defects in the Sr-layer due to RE substitution. Excess oxygen content is incorporated into the oxygen deficient Bi-O layers which makes it more insulating due to the RE substitution at higher concentrations. Thus, the Josephson coupling strength between the CuO$_2$ layers across the insulating layers becomes weaker at higher RE concentrations, which deteriorates the self- and in-field performance of RE substituted (Bi,Pb)-2212 at higher $x$. 

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6.4 Conclusions

In the present chapter, the magnetic field dependence of the n-indices is investigated, characterizing the E-J characteristics of RE-free and RE substituted (Bi,Pb)-2212 superconductor. The E-J characteristics are successfully explained by the flux-creep theory. It is found that the samples with n>15 and J<Jg show a glass-state for flux-lines, indicating their improved flux-pinning ability due to the creation of point defects by the substituted RE atoms. The behaviour is clearly seen from Uc as well. A correlation between n-indices and the Jc of RE substituted (Bi,Pb)-2212 superconductor is also observed. A deeper insight into the superconducting behaviour of RE substituted (Bi,Pb)-2212 superconductors has been obtained by comparing the self-and in-field n-indices. The highly enhanced n-value beyond 15 at applied fields under transport current flow shows that the modified material is a promising candidate for magnetic applications such as insert-magnets of high-field NMR.
References
