Properties of superconducting, polycrystalline dysprosium-doped Bi_{1.6}Pb_{0.5}Sr_{2-x}Dy_xCa_{1.1}Cu_{2.1}O_{8+x} (0 \leq x \leq 0.5)

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The structural and superconducting properties of dysprosium (Dy) doped (Bi,Pb)-2212 superconductor have been studied. Dy concentration is varied from x = 0.0 to 0.5 in a general stoichiometry of Bi_{n+1}Pb_{n+2}Sr_{2}Dy_xCa_{n+1}Cu_{2(n+1)}O_{8n+8}. It is found that the Dy atoms enter into the crystal structure by replacing Sr atoms and induce significant change in lattice parameter, microstructure, hole-concentration and normal state conductivity of the system. The critical temperature (Tc) and critical current density (Jc) of the Dy-doped samples enhance considerably at optimum doping levels. Maximum Tc of 92.3 K (for x = 0.4) and Jc of 1390 A/cm² at 64 K (for x = 0.2) are observed for doped samples as against 79.4 K and 127 A/cm², respectively, for the pure sample. The results are discussed on the basis of the change in hole-concentration due to Dy-doping at Sr-site of (Bi,Pb)-2212 superconductor.

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1. Introduction

Among the BSCO system of superconductors with the general formula Bi_{2}Sr_{2}Ca_{3}Cu_{4}O_{8}+d, the double layered cuprate (Bi,Pb)_{2}Sr_{2}Ca_{3}Cu_{2}O_{8+d} (n = 2) is of both fundamental and technological interest since it is amenable for processing of long length conductors with high critical current density (Jc) at 4.2 K and 10 T [11]. Since its discovery [2] extensive research work has been done to improve the structural and superconducting properties of the system. However, Bi-based superconductors are known for their strong anisotropic properties, very low charge carrier density, extremely short coherence length (ξ), and large penetration depth (λ). The inherent properties lead to unusually rapid flux creep which causes energy dissipation and to subsequent transition of superconductor to the normal state. The characteristic electric field (E)–current density (J) curves are closely related to the intrinsic properties, such as short coherence length and high two dimensionality of Bi_{2}Sr_{2}Ca_{3}Cu_{2}O_{8} (Bi-2212) [3–5]. The investigation of E–J characteristics is important not only from the aspect of basic physics but also from the applications point of view because of three basic reasons. Firstly, the critical current density (Jc) of Bi-2212 tapes or wires sensitively depends on the electric field criterion [6,7]. Secondly, the sharpness of the E–J curve is governed by the microstructural factors such as percolation of the superconducting current, weak coupling of grains, and precipitation of secondary phases rather than by the flux creep [8] and/or the glass liquid transition [3]. Finally, the slope of log E–log J curve should be large enough in order to obtain a large supercurrent with sufficiently low energy dissipation. Thus, precise measurements of E–J curves are essential, in order to identify Jc in a reasonable manner and for a better understanding of the relationship between the microstructure and current carrying properties of the superconductor for practical applications. Moreover, the carrier concentration in the Cu–O₂ planes strongly affects the superconducting transition temperature (Tc) [9]. The hole carrier density of the Cu–O₂ plane in Bi-2212 can be altered by changing the oxygen stoichiometry or by cationic substitution of divalent Ca/Sr in the active layers of Bi-2212 by a trivalent rare-earth (RE) elements. Hence, the properties of Bi-2212 superconductor can be tailored to suit for the application at higher temperature and fields [10,11]. The changes obtained by RE-substitution can also be used to investigate the mechanism of high Tc superconductivity [12–15]. In the case of Bi-2212, the substitution of Bi with Pb significantly improves the structural stability and slightly enhances Jc and the irreversibility field of the system [16–20]. Motohashi et al. reported that Pb in Bi-2212 single crystals increases the c-axis conductivity by significantly reducing anisotropy parameter γ [17]. Also Pb at Bi-site hinders the insertion of additional oxygen atom into the Bi-O double layers and hence the structural modulation becomes infinite, i.e., modulation-free condition. As a result anisotropy of modulation free crystals is strongly reduced [21].
Most of the previous RE-doping studies on Bi-2212 were done without Pb-doping at Bi-site [22–25]. In these cases, only marginal improvements in $T_c$ were observed even for optimum levels of RE, while there is no improvement of $J_c$ due to RE-doping. Our recent studies on co-doping of Pb and RE in Bi-2212 ([Bi,Pb]-2212) have shown significant improvements in the superconducting and flux pinning properties of Bi-2212 [26,27]. As a continuation of the above studies, the present work reports the significant changes in the structural and superconducting properties of (Bi,Pb)-2212 superconductor due to Dy-doping.

2. Experimental

Samples with the nominal stoichiometry of Bi$_{1.6}$Pb$_{0.5}$Sr$_2$Ca$_{1.4}$Cu$_{2.1}$O$_{x}$ (0 $\leq x \leq 0.5$) were prepared by solid-state synthesis using high purity oxides or carbonates, namely Bi$_2$O$_3$, PbO, SrCO$_3$, CaCO$_3$, CuO and Dy$_2$O$_3$ (Aldrich >99.9%). The accurately weighed ingredients using an electronic balance (Mettler AE240) were ground homogeneously using Agate balls and bowl in a planetary ball-mill (FRISCH Pulversette 6) for 2 h in acetone medium. The homogenous mixtures were kept in a muffle furnace with a uniform hot-zone area of 15 cm $\times$ 15 cm with temperature stability and accuracy better than $\pm$0.5 C. A programmable temperature controller (Eurotherm 2404) and a standard S-type thermocouple (NPL, UK) were used for the accurate monitoring and control of temperature. The samples underwent three stages of calcination in air at 800 C for 15 h + 815 C for 40 h + 880 C for 40 h with a heating rate of 3 C/min. Between each stage of calcination, the samples were ground in acetone medium to improve the homogeneity. The calcined powders were then pelletized (12 mm diameter and about 1 mm thickness) under a pressure of 500 MPa. The pellets were heat-treated for 120 h in two stages with a heat treatment schedule of 845 C for 60 h + 848 C for 60 h and a heating rate of 1 C/min with an intermediate pressing under the same pressure.

The structural and phase analyses of the samples were done using XRD (Philips Xpert Pro) equipped with an Xcelerator and a monochromator at the diffracted beam side (Step size: 0.0167°, Time per step: 45 s). Phase identification was performed using X'pert Highscore software in support with the ICDD-PDF2 database. The microstructure of freshly fractured surface of the samples were done using SEM (JEOL JSM 5600LV) with an accelerating voltage of 15 kV in secondary ion emission mode. The elemental analysis of the samples was done using EDX attached to SEM. The bulk density from 64 to 300 K was measured by conventional four-terminal method. The current and potential leads of high-grade copper wires were connected to the samples with silver coating, obtained by annealing silver paste at 600 C for 1 h on the surface of the samples. Cylindrical pellets were shaped into rectangular form with the dimensions 12 mm $\times$ 4 mm $\times$ 1 mm on which the potential leads, separated by a distance of 3 mm, placed at the central part of the specimen. The transport $J_c$ in self-field and $E$-$J$ characteristics of the samples under zero field and fixed fields namely, 0.32 and 0.64 T, were measured in a LN$_2$ bath cryostat with provision for vacuum at 64 K using four-probe method. A programmable temperature controller (Lakeshore 340) is used for the accurate monitoring of the temperature with a stability and accuracy of $\pm$0.01 K. The direction of current is parallel to the direction of pressed surface and the magnetic field is perpendicular to the pressed surface of the pellet. The current was ramped at a constant rate (1.0 A/ms) for the entire sample to avoid the influence of the ramp-rate on $E$-$J$ characteristics. Critical current ($I_c$) values of the samples were determined using a standard criterion of 1 $\mu$V/cm, derived from a resistance between voltage terminals. The $J_c$ values of the (Bi,Pb)-2212 were calculated from $I_c$ and the total cross-sectional area of the samples. The samples with different Dy stoichiometry such as 0.00, 0.10, 0.20, 0.30, 0.40 and 0.50 will be herein after denoted as SrDy0, SrDy1, SrDy2, SrDy3, SrDy4 and SrDy5, respectively.

3. Result and discussion

The XRD patterns of the samples after last-stage heat-treatment (Fig. 1) shows that both the pure and the Dy-doped samples contain the (Bi,Pb)-2212 phase only. No secondary phase containing Dy or any other cation is detected even up to $x = 0.5$. The absence of secondary phases supports that Dy is incorporated into the crystal structure of (Bi,Pb)-2212 superconductor. Lattice parameter variation of pure and Dy-doped samples is shown in Fig. 2, calculated by considering an orthorhombic symmetry for (Bi,Pb)-2212 system using the relation $1/d^2 = (h^2/a^2 + k^2/b^2 + l^2/c^2)$ [28]. With increase in Dy-content the $a$ and $b$ lattice parameters vary in such a fashion that they almost coincide at $x = 0.5$ showing that the orthorhombic symmetry of the system changes near to a pseudo-tetragonal symmetry. An increase in $a$-axis length is observed from $x = 0$ to 0.5 while $b$-axis length increases appreciably only up to $x = 0.2$ and thereafter remains more or less constant up to $x = 0.5$. The increase in $a/b$-axis length is associated with the increase in Cu–O bond length in Cu–O$_2$ planes, which controls the dimensions in the basal planes [25] of (Bi,Pb)-2212 system. A contraction in the $c$-axis length is also observed.
Table 1

Bulk density, Lotgering index, resistivity at 300 K and $\Delta T_C$ observed for pure and Dy-doped samples.

<table>
<thead>
<tr>
<th>Dy content</th>
<th>Cell volume (nm$^3$)</th>
<th>Bulk density ($\times 10^3$ kg/m$^3$)</th>
<th>Lotgering index, F</th>
<th>Resistivity at 300 K ($\mu\Omega$m)</th>
<th>$\Delta T_C$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.0</td>
<td>0.880</td>
<td>5.62</td>
<td>0.887</td>
<td>2.757</td>
<td>4.88</td>
</tr>
<tr>
<td>x = 0.1</td>
<td>0.887</td>
<td>5.55</td>
<td>0.752</td>
<td>2.814</td>
<td>7.75</td>
</tr>
<tr>
<td>x = 0.2</td>
<td>0.890</td>
<td>5.52</td>
<td>0.728</td>
<td>2.760</td>
<td>8.46</td>
</tr>
<tr>
<td>x = 0.3</td>
<td>0.892</td>
<td>5.47</td>
<td>0.681</td>
<td>6.322</td>
<td>8.87</td>
</tr>
<tr>
<td>x = 0.4</td>
<td>0.890</td>
<td>5.41</td>
<td>0.643</td>
<td>11.045</td>
<td>16.37</td>
</tr>
<tr>
<td>x = 0.5</td>
<td>0.893</td>
<td>5.36</td>
<td>0.557</td>
<td>15.113</td>
<td>18.97</td>
</tr>
</tbody>
</table>

with increase in Dy-content, indicating the incorporation of Dy atoms into the system. This is because in Bi-based cuprate superconductors, when a trivalent cation Dy$^{3+}$ (0.1052 nm) replace a divalent cation Sr$^{2+}$ (0.132 nm), additional oxygen in the Bi–O layers of the structure are incorporated in order to established the charge neutrality. As a result, the repulsion between Bi–O planes get reduced due to the reduction in the net positive charge in the Bi–O planes. This results in the contraction of Bi–O layers and causes the reduction of the c-axis length. The anisotropy of the system decreases with these changes in the lattice parameters [29]. The variation in lattice parameters results is also reflected in a slight increase in the cell volume (Table 1). The increase in cell volume is an evidence of oxygen implantation into the Dy-doped (Bi,Pb)-2212 system [30]. The XRD patterns of textured pellets and their well crushed and ground powder were used to calculate the Lotgering index ($F$) [31] (Table 1). It is observed that as the Dy-content increases, the texturing of (Bi,Pb)-2212 grains decreases monotonically, up to $x = 0.5$.

The SEM micrographs of freshly fractured surfaces of pure and Dy-doped (Bi,Pb)-2212 samples are shown in Fig. 3. The structural morphology of the samples varies with increase in $x$ value. The $x = 0$ sample shows clear and characteristic flaky grains revealing the layered growth mechanism, typical of (Bi,Pb)-2212. But, as $x$ value increases from $x = 0.1$ onwards the porosity of the samples increases slightly due to the disrupted grain growth. This leads to the reducing trend in the bulk density of the Dy-doped samples (Table 1). Considering the texturing or grain alignment of samples, $x = 0$ show a better structure compared to all other samples. EDX analysis was performed on number of large-flaky single-grain (spot analysis). It showed that the ratio of Dy/Sr in the (Bi,Pb)-2212 grains was almost equal to that of the corresponding starting composition for each $x$. The data also suggests that Dy substitutes on the Sr-sites in (Bi,Pb)-2212 system.

Fig. 3 shows the temperature dependence of resistivity ($\rho$–$T$) of pure and Dy-doped samples (0.0 ≤ $x$ ≤ 0.5). It is observed that all the samples show metallic behaviour above the $T_C$. The normal state resistivity (Table 1) of Dy-doped samples, namely $x = 0.1$ and $x = 0.2$ has almost identical values 2.814 $\mu\Omega$m and 2.760 $\mu\Omega$m, respectively. Beyond $x \geq 0.3$, it systematically increases with the increase in Dy-content to a maximum (15.113 $\mu\Omega$m) for $x = 0.5$ as against 2.757 $\mu\Omega$m for $x = 0$. The $T_C$ values measured from the $\rho$–$T$ plots using midpoint criterion are plotted against Dy content and the plots are shown in Fig. 5, which shows that $T_C$ increases considerably with increase in Dy-content and reaches a maximum for SrDy4 ($x = 0.4$) and then decreases. The $T_C$ increases from 79.4 K (SrDy0) to 92.3 K (SrDy4). The variation of $\Delta T_C$ ($T_{C-onset} - T_{C-zero}$) is given in Table 1, which shows that $\Delta T_C$ increases with increase in Dy-content up to $x = 0.5$ sample. The self-field $J_C$ also is found to increase significantly for Dy-doped samples [Fig. 5]. The pure sample shows a $J_C$ of 127 A/cm$^2$, while the maximum $J_C$ obtained is 1390 A/cm$^2$ for $x = 0.2$ sample at 64 K. This shows that the self-field $J_C$ of the sample at the optimum doping concentration ($x = 0.2$) is enhanced by almost 11 times as compared to pure sample ($x = 0$). It is also observed that the sample with $x = 0.4$ yields the maximum $T_C$, but its $J_C$ (324 A/cm$^2$) is less than that of the sample with $x = 0.2$. When Dy$^{3+}$ ions are substituted for Sr$^{2+}$, each substitution of Dy$^{3+}$ fills one hole in the crystal. Hence the hole-concentration in the Cu–O$_2$ plane decreases. When the Dy concentration reaches in the range 0.2–0.3, the system becomes optimally doped leading to enhanced $T_C$, $J_C$ and normal state conductivity. The $T_C$ is approximately consistent for $x = 0.3$–0.5.

Fig. 3. SEM micrographs of the pure and Dy-doped samples.
and $J_c$ changes in opposite directions for $x = 0.0 - 0.2$ and for $x = 0.2 - 0.5$. But the bulk density reduces slightly at a constant rate for the whole range of $x$. Thus it is concluded that $T_C$ and $J_c$ does not depend strongly on the microstructure.

To investigate the sharpness of the superconducting-normal state transition, the $E$–$J$ characteristics of pure and the Dy-doped samples were studied. The log $E$ vs. log $J$ curves of the samples at $0\, \text{T}$, $0.32\, \text{T}$ and $0.64\, \text{T}$ magnetic fields are shown in Fig. 6. The curves fit well (Fig. 6) with the equation $\log E = n \log J + C$, where $C$ is a constant and the $n$-index is the slope of these curves are shown

![Fig. 6. E–J curves of pure and Dy-doped samples.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_c$ (A/cm²)</th>
<th>n-Index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>Calculated</td>
</tr>
<tr>
<td>SrDy0</td>
<td>126.6</td>
<td>125.1</td>
</tr>
<tr>
<td>SrDy1</td>
<td>587.2</td>
<td>590.3</td>
</tr>
<tr>
<td>SrDy2</td>
<td>1392.8</td>
<td>1390.3</td>
</tr>
<tr>
<td>SrDy3</td>
<td>849.4</td>
<td>843.5</td>
</tr>
<tr>
<td>SrDy4</td>
<td>324.2</td>
<td>326.3</td>
</tr>
<tr>
<td>SrDy5</td>
<td>84.7</td>
<td>85.8</td>
</tr>
</tbody>
</table>

![Fig. 5. Variation of $T_C$ and $J_c$ of the samples with Dy-content.](image)

![Fig. 4. $\rho$–$T$ plots of pure and Dy-doped samples.](image)
in Table 2. In order to obtain a large supercurrent with sufficiently low energy dissipation, \( n \) value should be sufficiently high. In our case, we got linear curves with varying slope depending upon the Dy content. It is found that when Dy content increases the slope and hence the \( n \)-index increases and becomes maximum for SrDy2 in self- and applied-fields (Table 2). This shows that the sample, SrDy2 allows a maximum current with minimum dissipation of energy. This is clear from the calculated \( J_c \) values obtained from the linear fitting of \( \log E \) vs. \( \log J \) curves (Table 2).

4. Conclusion

The influence of Dy-substitution in (Bi,Pb)-2212 superconductor on the structure, \( T_c \), \( J_c \) and normal-state conductivity of the system has been studied. The XRD, EDX and the lattice parameter results supports the conclusion that the substitution takes place. The enhancements in the \( T_c \) and \( J_c \) are tremendous for Dy-doping in the range, \( x = 0.2–0.3 \). The \( x = 0.2 \) sample yields a \( J_c \) which is \( \sim 11 \) times higher than that of the pure sample, but the highest \( T_c \) is shown by the sample with \( x = 0.4 \). The enhancements are attributed to the shift in carrier concentration of the system from the overdoped to an optimally doped state. At higher Dy concentration all the above properties deteriorate due to the underdoped condition with respect to the hole density.

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