CHAPTER 5

METAL-INSULATOR TRANSITION AND TEXTURING
STUDIES OF RE (Pr, Y) SUBSTITUTED Bi-2212 CRYSTALS

5.1 Pr-SUBSTITUTED Bi-2212 BULK TEXTURED CRYSTALS

Bi-based superconductors are extensively studied by many groups. Among the various phases in the Bi-system, Bi-2212 phase exhibits good superconductivity and can be relatively easily synthesised in the form of bulk crystals when compared to Bi-2223 (Tohge et al 1989; Zhang and Hellstrom 1993; Tampieri et al 1994). Phase inhomogeneity and weak links are the major problems in the high $T_c$ superconductors. Large size crystals are very difficult to grow by the flux growth method. Texturing is an alternative way to get high $T_c$ as well as high $J_c$ values which can be achieved by different techniques like reactive sintering, high pressure pelletisation etc. (Li et al 1994).

The optimal carrier concentration is an important problem for the Bi-2212 phase and it can be varied either by substitution at different sites of Bi-2212 lattice or by annealing in different atmospheres like air, oxygen and argon (Yang et al 1993; Zhao et al 1995; Sun et al 1997b). Most of the substitutional studies have been carried out by solid state reaction through which the crystals will be having micron size grains. Metal insulator-transition (MIT) was observed in the case of 3-d metal and rare earth (RE) substitutions in the Cu and Ca site of Bi-2212 system respectively (Lonnberg et al 1992;
Agarwal and Narlikar 1994). MIT appears with different critical concentration ($x_c$) of RE substitutions (for Y:0.57, Nd:0.47, Gd:0.49, Ce:0.23 and Pr:0.49) with the variation of ±0.02 at% in the Bi-2212 system (Quitmann et al 1995).

Magnetic phase diagram of Pr doped Bi-2212 and Y:123 shows 0.5 at % substitution and gives rise to a sharp drop for both the systems (Gao et al 1992). In the Awana et al (1993) studies it was found that the $T_c$ depression rate was more for the Pr and Ce substituted samples compared to other RE substitutions and they claimed that the Pr ionic state is more than 3+. Detailed photo emission studies on MIT of Pr doped Bi-2212 polycrystalline samples were done by Quitmann et al (1995) and the interlayer coupling between Pr and Cu was discussed. The c-axis values of the Gd, Y, Er, and Dy doped samples decreased for the higher order dopants; but in the case of Pr doped samples the c-axis value remained unchanged (Awana et al 1993). For the Y doped single crystals a large discrepancy between melt composition and crystal composition was observed, but in the case of Pr doped samples so far there is no variation observed (Mitzi et al 1990; Villard et al 1997). In all the above Pr doped studies only polycrystalline samples were used and there is no report published so far on bulk textured crystal and the crystal chemical composition.

In the first part of this chapter, growth and characterisation of Pr substituted Bi-2212 bulk textured crystals have been discussed. The grown crystals have been characterised by optical microscope, SEM, XRD and AC susceptibility. Crystal chemical composition was analysed by ICP analysis and iodometry titration.

5.1.1 Experimental

The samples of Bi$_{2}$Sr$_{1.9}$Ca$_{1-x}$Pr$_{x}$Cu$_{2}$O$_{8+δ}$ (where $x$ =0.0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) compositions were prepared by standard solid state reaction technique.
The composition was selected according to Gopinath et al (1993) studies and 0.2 at % excess of Bi$_2$O$_3$ was added to compensate the evaporation losses during the process. Stoichiometric amounts of Bi$_2$O$_3$, SrCO$_3$, CaCO$_3$, CuO and Pr$_6$O$_{11}$ of purity greater than 99.9% were mixed with ethanol and ground in an agate mortar for 2 h. The mixture was calcined at 800 °C for 24 h. Since Pr substitution increases the melting point of the compound, second calcination was done at higher temperatures (840-860 °C) for 48 h with intermediate grindings. Sintered pellets (855-875 °C for 24 h) of size 40x5x5 mm$^3$ were used for the textured growth as feed material. Zone melting (predensification -10 mm h$^{-1}$ and crystal growth - 1 mm h$^{-1}$) was done using platinum strip heater floating zone system.

The melting point of the respective composition was observed by hot stage microscope setup using a platinum-rhodium wire heater and controlled by an Eurotherm temperature controller with an accuracy of ± 0.1 °C. The texturing quantification was done from the XRD intensity peaks using the Lotgering factor $F = (P-P_0) / (1-P_0)$, where $P$ is the sum of the XRD intensity ratio of $\sum I(00l)$ and $\sum I(hkl)$ and $P_0$ is the random sample equivalent parameter (Huang et al 1995). About 50 mg of the crystal was dissolved in 5 ml nitric acid and the solution was diluted to 25 ml to study the crystal composition using ICP method. $T_{c\text{onset}}$ and $T_{c\text{zero}}$ of the samples were observed from the temperature dependent AC susceptibility and electrical resistivity measurements.

5.1.2 Results and discussion

The grown bulk textured crystals of approximately 3.5cm length and 1cm diameter are shown in Figure 5.1. Figure 5.2 shows the discontinuity in the growth layers, which is due to fast cooling rate. The growth steps are also observed on the outer surface. The cleaved crystal surface of the inner core has no steps throughout the bulk. Absorption of gas bubbles into the fast pulled (predensification) bulk was due to
Figure 5.1 Some of the Pr substituted Bi-2212 as grown bulk textured crystals

Figure 5.2 Optical micrograph of layer steps observed on the outer surface of the as-grown undoped Bi-2212 crystal
less sintering temperature (Figure 5.3). Rotation rate also played an important role in the crystal growth. The optimal rotation rates were 20 rpm for the predensification and 10 rpm for the final growth. The final grown crystals (with a pulling rate of 1 mm h\(^{-1}\)) were aligned along the growth axis. The SEM picture of the cleaved crystals at the top surface is given in Figure 5.4. In the higher Pr content crystals, dark colour inclusions were observed as shown in the SEM picture (Figure 5.5). Single crystals could easily be cleaved from the bulk and were used for further studies. The melting points of the crystals were observed from the hot stage microscope and the values are given in the Table 5.1. The melting point of the Pr substituted crystal increases with increase of the Pr content. Higher level Pr substituted crystals form a gray colour needle-like structure while cooling from the molten state.

The XRD patterns of the grown crystals are given in Figures 5.6a and 5.6b. The cell parameters of the grown crystals were computed from the least square fitting method (with the error of \( \pm 0.003\text{Å} \)) and the values are given in Figure 5.7. Presence of (00l) peaks in the XRD patterns implies that the grown crystals are aligned to the growth axis. With the increase of Pr content the Lotgering factor \( F \) reduced and the values are given in the Table 5.1. This decrease in the texturing percentage was due to the formation of secondary phases in between the Bi-2212 layers and this was not observed in the XRD analysis (below the detection level). With increase of Pr content the c-axis value decreases and it confirms that Pr occupies the crystal structure (Prabhakaran and Subramanian 1997). A similar observation was also made in the Y, Gd, and Er doped samples (Yoshizaki et al 1990). The phase purity of the crystal decreased with the increase of substitution. In the predensified bulk, due to fast cooling rate a Bi-11905 secondary phase was observed. But in the finally grown crystals the X-ray peak intensities corresponding to Bi-11905 and Bi-free phases were observed only in the crystals substituted with higher Pr content (\( x>0.3 \)).
Figure 5.3  SEM picture of predensified Bi$_{2.2}$Sr$_{1.9}$Ca$_{0.8}$Pr$_{0.2}$Cu$_2$O$_{8+δ}$ sample

Figure 5.4  SEM picture of Bi$_{2.2}$Sr$_{1.9}$Ca$_{0.7}$Pr$_{0.3}$Cu$_2$O$_{8+δ}$ textured crystal cleaved from the top end of the bulk

Figure 5.5  SEM picture of gray colour inclusions observed in the Bi$_2$Sr$_{1.9}$Ca$_{0.4}$Pr$_{0.6}$Cu$_2$O$_8$ textured crystals
Figure 5.6a. XRD patterns of Bi$_{2.2}$Sr$_{1.9}$Ca$_{1-x}$Pr$_x$Cu$_2$O$_{8+y}$ textured crystals ($x = 0.0, 0.1$ and $0.2$)
Figure 5.6b. XRD patterns of Bi\textsubscript{2.2}Sr\textsubscript{1.9}Ca\textsubscript{1-x}Pr\textsubscript{x}Cu\textsubscript{2}O\textsubscript{8+y} textured crystals (x = 0.3, 0.4 and 0.5)
Figure 5.7 Cell parameter and $T_c$ values of $\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_x\text{Pr}_2\text{Cu}_3\text{O}_{8+y}$ textured crystals
Table 5.1

Transition temperature ($T_c$), Lotgering factor ($F$) and melting point of Bi$_{2.2}$Sr$_{1.9}$Ca$_{1.4}$Pr$_x$Cu$_{2}$O$_{8+y}$ textured crystal

<table>
<thead>
<tr>
<th>Pr value ($x$)</th>
<th>$T_c$ value (K)</th>
<th>Lotgering Factor $F$ (%)</th>
<th>Melting point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>87</td>
<td>73</td>
<td>860.0</td>
</tr>
<tr>
<td>0.1</td>
<td>80</td>
<td>75</td>
<td>864.3</td>
</tr>
<tr>
<td>0.2</td>
<td>70</td>
<td>69</td>
<td>867.7</td>
</tr>
<tr>
<td>0.3</td>
<td>65</td>
<td>63</td>
<td>870.4</td>
</tr>
<tr>
<td>0.4</td>
<td>52</td>
<td>60</td>
<td>874.9</td>
</tr>
<tr>
<td>0.5</td>
<td>33</td>
<td>57</td>
<td>878.1</td>
</tr>
<tr>
<td>0.6</td>
<td>ns</td>
<td>52</td>
<td>882.5</td>
</tr>
</tbody>
</table>

The chemical composition of the grown crystals was estimated by the ICP analysis and are normalised to the atomic ratio of Cu=2. A small piece of flux free single crystal was cleaved from the bulk and used for the analysis and the values are given in Table 5.2. Except Pr, remaining elements are having more or less the same value as that of initial composition. But the crystal composition of the substituted element (Pr) was less by about 0.025 at %.. Due to increase in the Pr content the Sr content decreases from 1.89 to 1.83 at%. A small variation in the Bi content was also observed with increase of Pr content. As the Pr content increases the Sr/Ca ratio increases from 2.01 to 3.74. A large variation in the Sr/Ca ratio was observed with increase of Pr content and hence the superconducting property of the crystal decreased. A trace of platinum metal into the final grown crystal lattice was observed (0.001 at%). The results of the oxygen estimation for the Pr substituted Bi-2212 bulk crystal is given in Table 5.2. From the measured values it is clearly evident that the oxygen content increased with increasing $x$ value. The excess oxygen will enter into the perovskite
block resulting in the decrease of repulsive force between the Bi-O double layers and this could be the reason for the suppression in superconducting properties.

Table 5.2

**Chemical composition of the Bi$_{2.2}$Sr$_{1.9}$Ca$_{1-x}$Pr$_{x}$Cu$_{2}$O$_{8+y}$ textured crystals**

<table>
<thead>
<tr>
<th>Pr ($x$) (starting)</th>
<th>Crystal composition (normalised to Cu=2.0)</th>
<th>Sr/Ca ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>Bi: 2.17, Sr: 1.89, Ca: 0.94, Pr: 0.00, O: 8.10</td>
<td>2.01</td>
</tr>
<tr>
<td>0.1</td>
<td>Bi: 2.16, Sr: 1.87, Ca: 0.82, Pr: 0.07, O: 8.13</td>
<td>2.28</td>
</tr>
<tr>
<td>0.2</td>
<td>Bi: 2.12, Sr: 1.88, Ca: 0.70, Pr: 0.11, O: 8.19</td>
<td>2.68</td>
</tr>
<tr>
<td>0.3</td>
<td>Bi: 2.13, Sr: 1.85, Ca: 0.58, Pr: 0.23, O: 8.26</td>
<td>3.19</td>
</tr>
<tr>
<td>0.4</td>
<td>Bi: 2.10, Sr: 1.79, Ca: 0.53, Pr: 0.31, O: 8.33</td>
<td>3.38</td>
</tr>
<tr>
<td>0.5</td>
<td>Bi: 2.07, Sr: 1.85, Ca: 0.51, Pr: 0.39, O: 8.41</td>
<td>3.63</td>
</tr>
<tr>
<td>0.6</td>
<td>Bi: 2.11, Sr: 1.83, Ca: 0.49, Pr: 0.47, O: 8.49</td>
<td>3.74</td>
</tr>
</tbody>
</table>

The AC susceptibility data of the grown crystals are shown in Figure 5.8. The Pr substitution suppresses the superconducting property and this is due to hole filling mechanism as stated by Awana et al (1993). Due to the extra oxygen in the Bi-O plane the transition width of the Pr substituted crystal increases accordingly. MIT was observed for the textured crystal of $x=0.6$ substitution, but the corresponding crystals composition showed only $x=0.47$. Superconducting to metallic transition was observed up to $x=0.4$. The $x=0.5$ substituted samples show superconductivity at low temperature because of longer coherence length as explained by Ma and Lee (1985). Crystals with higher Pr content ($x=0.6$) lead to semiconducting behaviour at low temperature. The presence of a higher order Pr ($x>0.6$) element in the crystal structure localises the charge
Figure 5.8 Temperature dependence of AC susceptibility for Bi$_{2.2}$Sr$_{1.9}$Ca$_{1-x}$Pr$_x$Cu$_2$O$_{8+8}$ textured crystals
carriers which leads to MIT at low temperature. The resistivity measurements of the crystals show a very sharp transition at the $T_c$ zero point (Figure 5.9) and the values are given in Table 5.1.

5.2 GROWTH OF $\text{Bi}_{2.2}\text{Sr}_{1.5}\text{Ca}_{1-x}\text{Y}_x\text{Cu}_{2}\text{O}_{8+y}$ BULK TEXTURED CRYSTALS

High $T_c$ bismuth cuprate superconductors are anisotropic in nature and their current carrying capacity is much higher along the a-b plane than in the c-plane (Han et al 1997). Recently high $T_c$ superconducting textured thick films were realised in the field of microelectronics, because of their potential applications such as, microwave filters, resonators and antennas (Alford et al 1997; Gallop 1997). The suppression of superconductivity with rare earth substitution in the Bi-2212 system has engaged the attraction of many research groups who have studied the various physical properties of the system and tried to understand them (Gopinath et al 1993; Quitmann et al 1995). In the Er doped system the suppression of superconductivity due to disorder was explained with Ortuno and Pollak model (Sattar et al 1996).

Rare earth substitutions like Y increase the oxygen ratio in the Bi-O plane and also the modulation structure was reported by Kambe et al (1995). Due to different processing techniques and dopants, apart from CuO and Bi-2201 phases, variety of nonsuperconducting phases like $(\text{Ca},\text{Sr})_2\text{CuO}_3$, $\text{Bi}_2\text{Sr}_2\text{CaO}_8$, $\text{Bi}_{2.2}\text{Sr}_{2.8}$ and $\text{Bi}_2\text{Sr}_{1.7}\text{Ca}_3\text{O}_8$ were identified in between the superconducting grains (Majewski 1997). Stassen et al (1996b) studied the texturing nature of the Dy doped Bi-2212 polycrystalline sample by applying (1.2 T) magnetic induction during the process and it ended up with a multi-phase textured compound.

In the Y and La doped Bi-2212 single crystal growth, the dopant composition in the crystal was found to be two to three times higher than the initial composition and the reason was explained in detail (Mitzi et al 1990; Kendziora et al
Figure 5.9 Resistivity versus temperature of Bi$_{2.2}$Sr$_{1.9}$Ca$_{1-x}$Pr$_x$Cu$_2$O$_{8+x}$ textured crystals
1992). Gao et al (1992) reported that the extra hole substitution by the dopant occupies the Cu-O plane and breaks the hybridisation of the Cu 3d-O 2p states within the CuO planes. Rare earth substituted Bi-2212 texturing was not well studied, whereas a few studies on thin and thick textured films of the pure Bi-2212 system were reported (Dimesso et al 1991; Ishibashi et al 1994). Haugan et al (1995) have reported that the texturing, phase formation and critical current density of the as-grown crystals were enhanced by heat treatment. Texturing analysis of Bi-2212 tapes were done by neutron diffraction studies and the texturing was found to be very strong (Wenk et al 1996). It has been reported that the addition of MgO and SrSO4 reduces the Sr-Ca-Cu-O secondary phase inclusion and it enhances the texturing nature of the Bi-2212 thick film (Huang et al 1996). Incorporation of Y in the Bi-2212 crystal was high when compared to the initial ratio of the powder and Villard et al (1997) reported the optimum Y content in the Bi-2212 system for the maximum \( T_c \) value.

The results obtained for the Y substituted textured Bi-2212 crystals grown by platinum strip heater floating zone technique is reported in the following part of this Chapter. Morphology, structural and chemical composition of the grown crystals were analysed. Resistivity studies have been done by using four-probe method along the growth direction of the crystal. Etching studies reveal the twinning in the crystal.

5.2.1 Experimental procedure

Bulk textured crystals of Bi\(_{2.2}\)Sr\(_{1.9}\)Ca\(_{1+\delta}\)Y\(_x\)Cu\(_{2}\)O\(_{8+\delta}\) (0 ≤ \( x \) ≤ 0.6 in steps of \( x = 0.1 \)) were grown by platinum strip heater floating zone technique. Stoichiometric amounts of powders Bi\(_2\)O\(_3\), SrCO\(_3\), CaCO\(_3\), CuO and Y\(_2\)O\(_3\) of purity greater than 99.9% were mixed with ethanol. The mixture was calcined first at 800-825 °C for 24 h. After grinding, subsequent calcination was done at 845-860 °C for 48 h. The feed rods were prepared in the form of rectangular pellets of size 40x5x5 mm\(^3\). The green pellets were
sintered at 855-875 °C for 24 h in a pure alumina boat. Sintered pellets were predensified at a faster pulling rate (10 mm h\(^{-1}\)) and the crystal growth was done at a slower rate (1 mm h\(^{-1}\)) with a rotation rate of 10 rpm. The grown crystals were cut and polished along the growth direction and used for further characterisation. AFM studies were done for the as grown cleaved crystals. Four different types of etchants were tried for this study and the corresponding compositions are 1% Br₂-methanol, HCl-H₂O (1:4), HCl-methanol-acetic acid (1:4:4) and HNO₃-methanol-acetic acid (1:4:4).

5.2.2 Results and discussion

Some of the as-grown bulk crystals are shown in Figure 5.10. During predensification (10 mm h\(^{-1}\)) some of the air or vapor gases got into the material and micro-pores were formed inside the bulk. Finally these micro-pores combine together and form a hollow space during crystal growth (1 mmh\(^{-1}\)) and the cross cut of one such predensified and slow pulled crystal is shown in Figure 5.11. This can be overcome by the proper processing method and high density packing (sintering). The texturing alignments of the crystals were examined along the growth direction as well as perpendicular direction using SEM and one such parallel view is shown in Figure 5.12. The optimum rotation rate is 10 rpm and with the increase of the rotation rate, the temperature of the melt region decreased and hence the shape tends to be irregular. Single crystals of size about 7x4x0.05 mm\(^3\) were cleaved from the bulk and used for the characterisation studies. Increase of Y content leads to Bi-free secondary phase (black in colour) present in between the superconducting phase. The optical micrograph (Figure 5.13) shows the layered structure on the outer surface of the crystal along with Bi-free phase for x= 0.6.

Microstructural evaluation of oxide superconductors are very much essential. Since superconducting oxides are ceramic and brittle in nature, the studies of
Figure 5.10  Some of the bulk textured Bi$_{2.2}$Sr$_{1.9}$Ca$_{1.4}$Y$_{0.6}$Cu$_2$O$_{8+\delta}$ crystals

Figure 5.11  Cross cut view of bulk predensified and final grown crystal
Figure 5.12  SEM picture of cleaved surface of Bi$_{2+}$Sr$_{1.9}$Ca$_{1.9}$Y$_{0.1}$Cu$_2$O$_{8+5}$ (arrow indicates the growth direction)

Figure 5.13  Layer pattern observed on the outer surface of the Bi$_{2+}$Sr$_{1.9}$Ca$_{0.1}$Y$_{0.0}$Cu$_2$O$_{8+5}$ crystal with dark secondary phases
deformation and fracture mechanism are needed. In the present study, AFM was used for revealing the growth layers of Y substituted Bi-2212 bulk textured crystals. In the undoped Bi-2212 system, the cleaved bulk crystal shows that the layers are parallel to the growth direction with clear growth front as shown in Figure 5.14a and the a-b plane is aligned along the growth direction. As the Y percentage increased in the Bi-2212 system, due to the formation of secondary nonsuperconducting phases, the a-b plane gets misoriented and the growth front is uneven as shown in Figure 5.14b. The melting point of the Y substituted textured crystal was determined from the DTA curve (Figure 5.15). From the curve it is clear that the melting point of the crystal increased from 841.4 to 884.7 °C with respect to Y.

Cell parameter values of the grown crystal were calculated from the XRD patterns and it was found to be of orthorhombic structure. Since the atomic radius of Y is small compared to the Ca atom, the c-axis values of the Y substituted crystal decreased with increase of Y content. The value of the a-axis was found to be slightly decreased with respect to Y content as shown in Figure 5.16. The grown crystals were aligned along the growth direction and the corresponding XRD patterns are shown in Figures 5.17a and 5.17b. The texturing nature decreased from 64% to 30%, due to the increase of Y substitution. This reduction was due to secondary phase formation in between the Bi-2212 layers as shown in Figure 5.18. Secondary superconducting Bi$_{11-}Sr_9Cu_{50}x$ (Bi-11905) phase was observed for the x>0.3 crystals and non superconducting Sr$_6$Ca$_{12}$Cu$_{24}$O$_{y}$ (Bi-free) phase was found only for x > 0.4 crystals. The phase purity of the Y doped crystal decreased from 98% to 66% as the Y content increases (Figure 5.18). XRD analysis showed no peaks corresponding to Bi-2201 or Y$_2$CuO$_4$ phase found in the higher order Y substituted crystals.

Chemical composition of the grown crystals was quantified from the ICP analysis and the results are given in Figure 5.19 (values were normalised to Cu=2 ratio). For a lower value of Y substitution, the Y content in the crystal was found to be
Figure 5.14a  AFM picture of undoped Bi-2212 textured crystal

Figure 5.14b  AFM picture of Y substituted (x=0.6) Bi-2212 textured crystal
Figure 5.15 DTA curve of Bi$_{2.2}$Sr$_{1.9}$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+y}$ textured crystals
Figure 5.16 Cell parameter values of Bi$_{2.2}$Sr$_{1.9}$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+\delta}$ versus Y content (x)
Figure 5.17a XRD patterns of Bi$_{22}$Sr$_{19}$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+y}$ textured crystals ($x=0.0, 0.1$ and $0.3$)
Figure 5.17b XRD patterns of Bi$_2$Sr$_{1.9}$Ca$_{1.4}$Y$_x$Cu$_2$O$_{8+y}$ textured crystals ($x=0.4, 0.5$ and $0.6$).
Figure 5.18 Texturing percentage, \( T_{\text{onset}} \) and Bi-2212 phase purity of \( \text{Bi}_{2.2}\text{Sr}_{1.9}\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+\delta} \) versus Y content (x)
Figure 5.19 Chemical composition of $\text{Bi}_2\text{Sr}_{1.9}\text{Ca}_{1.4}\text{Y}_x\text{Cu}_2\text{O}_{8+\delta}$ with respect to Y content (x)
1.5 to 3 times higher than that of the nominal composition. This initial increase of Y in the crystal enhances the oxygen content in the crystal thereby increasing the superconducting property. At still higher order substitution, the incorporation of Y into the crystal was found to be decreased (Prabhakaran and Subramanian 1998b). Small variation in the Bi and Sr content was observed and it was not uniform throughout the bulk.

A superconducting property of the grown crystals was characterised using the four-probe method and the values are given in Figure 5.20. The measurements were taken along the growth direction of the crystal. Due to lower Y content in the crystal, first the $T_c$ was found to be increased from 87 K to 89 K and then it decreased enormously for the higher values of Y substitution. The $\Delta T_c$ was found to be sharp (< 8 K) up to $x=0.3$ and then it increased to higher values (Table 5.3). Semiconducting behavior was observed for the $x=0.6$ crystal. From the iodometry titration, the oxygen contents of the crystals were quantified and the results are given in Table 5.3. Oxygen content was found to be increased from 8.10 to 8.42 at% for the Y substituted crystals, due to the electronic charge difference.

Among the etchants used, Br$_2$ mixture was found to be very effective whereas other etchants were very slow in reactive nature. Etching studies revealed the micro-twinning along the growth axis and the etching time was less than 1 min. Figure 5.21 shows the etch pattern of the cleaved surface along the growth axis of the $x=0.5$ crystal and the dark colour appearance may be secondary phase.

5.3 IRRADIACTION STUDIES ON NONSUPERCONDUCTING Y ($x=0.6$) SUBSTITUTED Bi-2212 TEXTURED CRYSTAL

In order to improve the superconducting property of Bi based cuprates, different dopants were used for preparing the phase pure material. Because of
Figure 5.20  Resistivity versus temperature plot of Bi$_2$Sr$_{1.9}$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+\delta}$ bulk textured crystal
### Table 5.3

**Transition width and oxygen content of Y substituted crystals**

<table>
<thead>
<tr>
<th>Y content (x)</th>
<th>$\Delta T_c$ (K)</th>
<th>Oxygen content ($O_{8+y}$)</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>6</td>
<td>8.10</td>
<td>841.4</td>
</tr>
<tr>
<td>0.1</td>
<td>5</td>
<td>8.08</td>
<td>846.2</td>
</tr>
<tr>
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<td>7</td>
<td>8.16</td>
<td>851.8</td>
</tr>
<tr>
<td>0.3</td>
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<td>8.21</td>
<td>859.9</td>
</tr>
<tr>
<td>0.4</td>
<td>12</td>
<td>8.29</td>
<td>868.3</td>
</tr>
<tr>
<td>0.5</td>
<td>18</td>
<td>8.36</td>
<td>876.4</td>
</tr>
<tr>
<td>0.6</td>
<td>&gt;30</td>
<td>8.42</td>
<td>884.7</td>
</tr>
</tbody>
</table>
Figure 5.21 Etch pattern of Bi$_{2.2}$Sr$_{1.9}$Ca$_{0.5}$Y$_{0.5}$Cu$_2$O$_{8+\delta}$ crystal along the growth direction.
incongruent melting of these materials, it is very difficult to produce them in large single 
crystal form (Oka et al 1993). Moreover, after growth it reacts with the atmosphere and 
the superconducting property gets reduced (Wei et al 1993). Low level of gamma ray 
irradiation enhances the $T_c$ onset of BSCCO thin film from 63 K to 85 K (Ishibashi et al 
1994). Significant improvement in the $T_c$ value and the narrowing of the transition 
width ($\Delta T_c$) were explained on the basis of anisotropy reduction (Gao et al 1995b).

The effective pinning centers at low temperatures are believed to be mainly 
due to the oxygen vacancies in the CuO$_2$ plane (Pradhan et al 1996b). Konczykowski et 
al (1991) studied the 5.3 GeV Pb ion irradiation at room temperature and showed the 
increase of hysteresis loop upon irradiation in the YBCO crystals. Most of the irradiation 
investigations were done on pure Bi-2212 system and there is no report available on the 
highly doped Bi-2212 crystal.

The author investigated the heavily Y substituted (60 mol %) to the Cu site 
of Bi-2212 crystals grown by floating zone techniques for the irradiation studies. 250 
MeV of Ag$^{17+}$ energy source with different dosages of flux were irradiated on the crystals 
at room temperature. The superconducting property of the as grown and irradiated 
crystals was measured using AC susceptometer. The change in the chemical 
composition was studied using ICP and iodometry titration methods.

5.3.1 Irradiation procedure

For the irradiation studies Y substituted Bi-2212 crystals with composition 
of Bi$_{12.2}$Sr$_1$Y$_{0.4}$Ca$_{0.4}$Cu$_{2}$O$_{8+6}$ were used. After surface examination flux free crystal
was used for further measurement. The irradiation (250 MeV $^{17+}$ ions) was done with two different dosages ($2.5 \times 10^{10}$ and $5 \times 10^{10}$ ions cm$^{-2}$) in the present study.

5.3.2 Results and discussion

In the Y substituted Bi-2212 as grown crystals, positive $\chi''$ values observed due to semiconducting nature at low temperature the AC susceptibility are given in Figure 5.22. A small negative $\chi'$ was noticed at around 60 K due to the presence of thin layer of Bi-2212 phase in the bulk. Incommensurate state appears due to excess oxygen in the Bi-O plane for the higher order Y substitution. As the crystals were subjected to irradiation, due to removal of oxygen, semiconducting property decreased. For $2.5 \times 10^{10}$ ions cm$^{-2}$ dosage of irradiation, the volume fraction of Bi-2212 phase increased and the $T_c$ onset value shifted to around 80 K. For further increase of irradiation dosage ($5 \times 10^{10}$ ions cm$^{-2}$), semiconducting property transformed to metallic.

Because of the irradiation process, oxygen content decreased from 8.42 at% to 8.31 at% for the crystal irradiated at $5 \times 10^{10}$ ions cm$^{-2}$. Whereas there was no variation observed for the rest of elements in the crystal. Over a period of time (three months) the oxygen content of the irradiated crystal increased due to absorption from the atmosphere and it became nonsuperconductor. STM studies on these crystals show that as the dosage increased the corresponding columnar defects produced also increased. Even though the dosage of the irradiation is small ($<10^{11}$ ions cm$^{-2}$), the superconducting property of the material changed due to the small variation in the oxygen content in the bulk.
Figure 5.22  Temperature dependence AC susceptibility for as grown and irradiated Bi$_{2.2}$Sr$_{1.9}$Ca$_{0.4}$Y$_{0.6}$Cu$_{3}$O$_{6+8}$ textured crystal
5.4 CONCLUSIONS

Bulk textured $\text{Bi}_{22} \text{Sr}_{1.9} \text{Ca}_{1-x} \text{Pr}_{x} \text{Cu}_{2} \text{O}_{8+y}$ (0.0 ≤ x ≤ 0.6) crystals have been grown at a rate of 1 mm h⁻¹ pulling rate. Higher order Pr substitution increase the melting point of the compound and secondary phases (for x ≥ 0.4) were observed in between the superconducting Bi-2212 layers. Incorporation of Pr into the Bi-2212 textured crystal was confirmed by chemical analysis and the oxygen content increased with respect to Pr substitution level. Superconducting nature vanished and texturing ratio decreased for the higher level of substitution.

Bulk textured crystals of $\text{Bi}_{22} \text{Sr}_{1.9} \text{Ca}_{1-x} \text{Y}_{x} \text{Cu}_{2} \text{O}_{8+y}$ (0.0 ≤ x ≤ 0.6) have been grown using optimum growth conditions. Texturing ratio of the grown crystal decreased from 64% to 30% with increase of Y substitution. Secondary non-superconducting phase formation decreases the texturing and superconducting nature with respect to Y substitution. Incorporation of Y into the crystal raised the oxygen content from 8.10 at% to 8.42 at% with respect to Y substitution. Micro twinning in the bulk texture crystal was realized along the growth direction during etching.

Irradiation studies on the $\text{Bi}_{22} \text{Sr}_{1.9} \text{Ca}_{0.4} \text{Y}_{0.6} \text{Cu}_{2} \text{O}_{8+y}$ bulk textured crystal was done using two different dosages (2.5x10¹⁰ and 0.5x10¹⁰ ions cm⁻²). Due to the removal of oxygen content from the irradiated bulk textured crystal, semiconductor to metallic nature was appeared during cooling the sample.