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# A Novel Technique for the Preparation of Textured $YBa_2Cu_3O_{7-\delta}$ Superconductor

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**Abstract**

Textured samples having composition of $YBa_2Cu_3O_{7-\delta}$ were prepared by using a novel technique of heating the samples in a thermal gradient which varies linearly between 930-950 °C over a distance of 5 cm. The samples were characterized by X-ray powder diffraction analysis, temperature dependent resistivity and magnetic susceptibility measurements, and scanning electron microscopy.

XRD analysis shows that sample heated between 930-935 °C has tetragonal symmetry and all other three samples show orthorhombic symmetry. Samples heated in temperature gradient of 935-945 °C aligned along the c-axis. The orthorhombic samples exhibited zero resistance above 86K with short transition width and samples heated in the temperature range of 930-935 °C was non-superconducting down to 80 K. Susceptibility measurements also confirms the same $T_c$ values for the superconducting samples. The orientation of crystals and alignment of grains was observed by SEM images and investigated by XRD patterns. The maximum texture alignment of the $YBa_2Cu_3O_{7-\delta}$ superconducting grains is obtained in a thermal gradient of 935-945 °C.

## 1. Introduction

Single crystal orthorhombic $YBa_2Cu_3O_{7-\delta}$ shows anisotropic transport properties which are quite different along the c-axis [1]. It is difficult to investigate these properties, because the size of its single crystal is small and very thin. It is therefore, imperative that their properties be studied on oriented polycrystals which may show new features of superconducting oxides. Despite various publications [2] on (what is generally termed) the textured growth of 123 YBCO there is still a relatively limited information on the textured growth process.

Conventionally sintered $YBa_2Cu_3O_{7-\delta}$ (123) compounds display a low current density due to weak-links related to high angle grain boundaries. One of the best prospects for obtaining high critical current densities ($J_c$) in $YBa_2Cu_3O_{7-\delta}$ (123) is to orient the grains in such a way that the high $J_c$ (i.e. a-b) plane is aligned in the direction of current flow.

Several studies [3-6] have succeeded in reducing the weak link problem by employing a melt and directional solidification process which enables the fabrication of well textured samples with clean boundaries and large grains in a preferred orientation. These samples have dramatically improved transport $J_c$ values at the boiling point of liquid nitrogen above $10^5$ A/cm$^2$ in zero magnetic field (H) and of above $10^3$ A/cm$^2$ at H=1 T compared to a value of several hundred and about 1 A/cm$^2$, respectively, for those samples without texturing. Single crystal of orthorhombic $YBa_2Cu_3O_{7-\delta}$. [7] shows anisotropic transport properties which are quite different along the c-axis.

Techniques such as uniaxial pressing and sintering [8], applying magnetic field [9] during horizontal unidirectional solidification of $YBa_2Cu_3O_{7-\delta}$, melt texturing [10] and gradient firing [11-15], show promise for achieving the highly textured microstructure for bulk 123 superconductors.

In this paper, we report the preparation of preferably oriented orthorhombic polycrystals of $YBa_2Cu_3O_{7-\delta}$, by using a novel technique of heating in the presence of a temperature gradient.

## 2. Experimental Procedure

Samples with composition $YBa_2Cu_3O_{7-\delta}$ were prepared by thermal treatment under a gradient of 20 °C spread over a distance of 5 cm starting from 930 °C. Stoichiometric mixtures were prepared by using $Y_2O_3$, $BaCO_3$ and CuO powders of purity better than 99.9 %. The powders were ground, mixed and pelletized under uniaxial pressure before heating. The first heating at 900 °C was performed in a uniformly heated zone for 16 hours. The product from the first heating was reground and pressed into four pellets (P1-P4) having diameter of 1.0 cm each. These pellets were placed in a multizone tube furnace with a thermal gradient of 20 °C which vary linearly such that the temperature gradient increases from sample P1 to P4. These pellets were subjected to a heating cycle of 16 hours in air and then in flowing oxygen for another 16 hours. Afterwards, they were slowly cooled to 200 °C at a rate 1 °C/min, also in flowing oxygen in the thermal gradient from 930-950 °C. These pellets were heated again at a fixed temperature of 915 °C for 12 hours, in air and then slowly cooled to 470 °C and heated for 8 hours and then slowly cooled to room temperature.

The superconductivity transition temperatures were measured using four-probe method with dc current of 4.98 mA. Contacts were made with thin copper wires by using silver paint. The voltage drop across the two inner electrical contacts were measured against temperature. X-ray diffraction was carried out by powder diffraction method at room temperature using a Rigaku XRD D/MAX-IIA diffractometer using Cu-$K_\alpha$ radiation, with scanning speed of $1°(2\theta)$/min.

A.C. susceptibility measurements were made with the magnetic field either parallel or

perpendicular to the faces of rectangular pellets, by using a sensitive A.C. setup employing mutual inductance method. Measurements were made at a field of 0.5 Oe and lock-in frequency for this measurement was 200 Hz and temperature variation was measured by using copper-constantan thermocouple.

The microstructure analysis was carried out using a high resolution scanning electron microscope operated at 25 KeV in a secondary electron image mode.

## 3. Results and Discussion

X-ray diffraction pattern in Figure 1 shows that Sample-P1 belongs to tetragonal phase of $YBa_2Cu_3O_{7-\delta}$ along with some impurity peaks ($\Delta$) around $2\theta = 28.15°$, 29.05°, 29.57°, 29.9° and 31.07°. Some of these impurity peaks can be indexed for $Y_2BaCuO_5$ (211) phase which were suppressed after last heating.

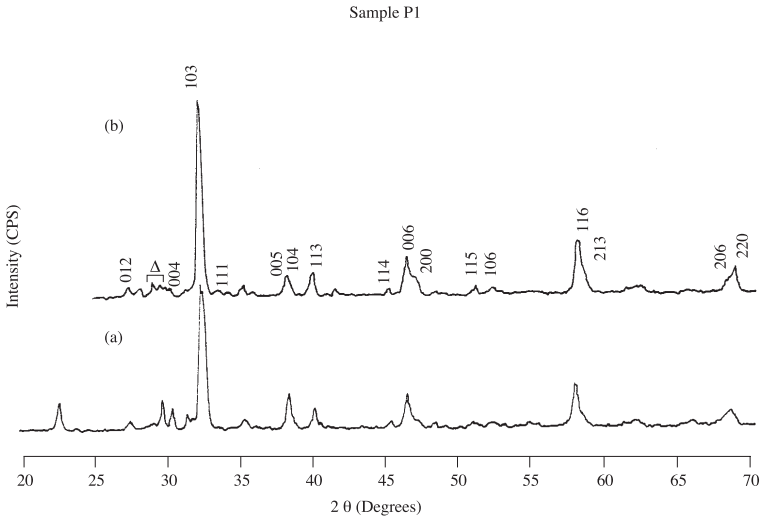



**Figure 1.** XRD patterns of sample P1: a. after 3rd heating b. after last heating

Figures 2-3 show x-ray diffraction pattern of samples P2 and P3 which had been heated in temperature ranges of 935-940 °C and 940-945 °C, respectively. These patterns can be indexed according to the orthorhombic phase. The sharpness of the peaks indicates that the sample consists of well developed crystallites which are aligned in some particular direction. In Figures 2-3 it is obvious that relative intensities due to the (00l) plane increased remarkably during the last heating. Texture coefficients (T.C.) for the crystal planes for samples P2-P4 are calculated by using the formula

$$T.C. = \frac{I_{(hkl)}/I_0(hkl)}{\frac{1}{N}\sum_{1}^{N} I_{(hkl)}/I_0(hkl)}, \tag{1}$$

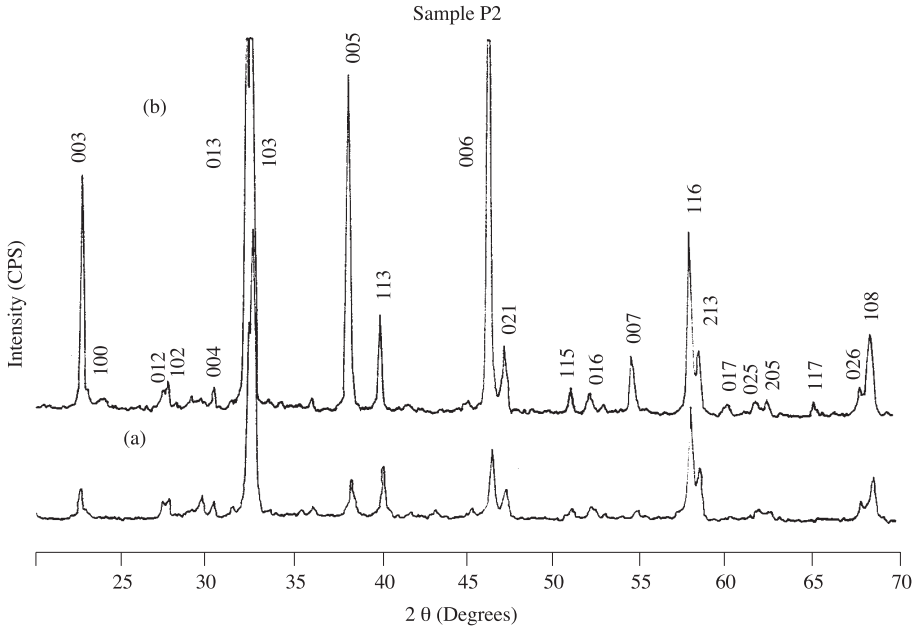



**Figure 2.** XRD patterns of sample P2: a. after 3rd heating b. after last heating

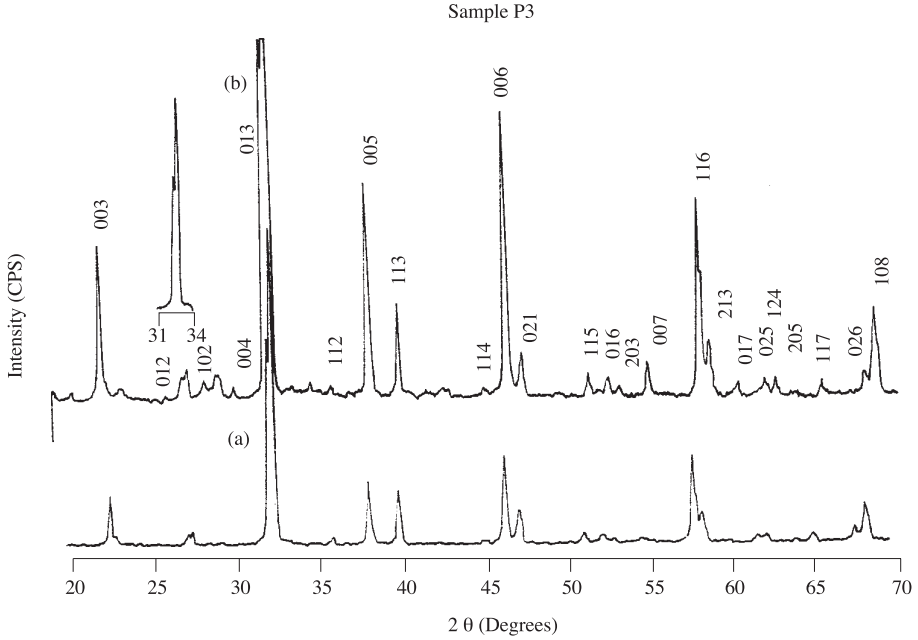



**Figure 3.** XRD patterns of sample P3: a. after 3rd heating b. after last heating

where $I_0$ is the standard value of intensity for the respective peak [16]. Texture coefficients of respective planes for P2 is given in Table 1, whereas a comparison of T.C.'s for samples P2-P4 is provided in Table 2. The values of texture coefficients for (00l) have remarkably increased for P2 with relatively lower values for P3.

X-ray diffraction pattern for sample P4, which was heated in temperature gradient of 945-950 °C, shown in Figure 4, can also be indexed for orthorhombic phase $YBa_2Cu_3O_{7-\delta}$. The intensity and texture coefficients of diffraction lines for P4 do not show any remarkable increase in their values as indicated in Table 2. Therefore, it may be concluded that at this temperature range no significant texture alignment takes place.

**Table 1.** X-Ray Diffraction Data for Sample P2.

| Sr. No. | hkl | $2\theta$ | d | I | $I_0$ | $I/I_0$ | T.C. |
|---|---|---|---|---|---|---|---|
| 1 | 003 | 22.70 | 3.905 | 43.30 | 10 | 4.330 | 2.597 |
| 2 | 100 | 23.12 | 3.846 | 3.07 | 4 | 0.767 | 0.460 |
| 3 | 012 | 27.50 | 3.243 | 3.23 | 3 | 1.076 | 0.646 |
| 4 | 102 | 27.79 | 3.210 | 4.46 | 5 | 0.892 | 0.535 |
| 5 | 004 | 30.50 | 2.931 | 3.84 | 1 | 3.840 | 2.303 |
| 6 | 013 | 32.48 | 2.756 | 90.77 | 55 | 1.650 | 0.984 |
| 7 | 103 | 32.74 | 2.735 | 100.0 | 100 | 100 | 0.600 |
| 8 | 111 | 33.75 | 2.655 | 1.15 | 2 | 0.575 | 0.345 |
| 9 | 112 | 36.28 | 2.476 | 1.92 | 3 | 0.640 | 0.384 |
| 10 | 005 | 38.48 | 2.339 | 63.85 | 13 | 4.911 | 2.946 |
| 11 | 113 | 40.30 | 2.238 | 17.84 | 14 | 1.272 | 0.764 |
| 12 | 006 | 46.58 | 1.950 | 98.46 | 22 | 4.475 | 2.684 |
| 13 | 200 | 47.50 | 1.915 | 12.30 | 12 | 1.025 | 0.615 |
| 14 | 115 | 51.41 | 1.777 | 4.46 | 4 | 1.115 | 0.666 |
| 15 | 016 | 52.48 | 1.743 | 3.54 | 3 | 1.180 | 0.658 |
| 16 | 203 | 53.30 | 1.713 | 1.38 | 2 | 0.690 | 1.667 |
| 17 | 007 | 54.96 | 1.670 | 10.60 | 2 | 5.300 | 3.179 |
| 18 | 116 | 58.19 | 1.585 | 34.86 | 26 | 1.340 | 0.804 |
| 19 | 213 | 58.70 | 1.573 | 12.30 | 13 | 0.946 | 0.567 |
| 20 | 107 | 60.40 | 1.532 | 2.30 | 1 | 2.300 | 1.379 |
| 21 | 025 | 62.00 | 1.497 | 2.00 | 2 | 1.000 | 1.667 |
| 22 | 205 | 62.67 | 1.482 | 2.30 | 3 | 0.766 | 0.459 |
| 23 | 117 | 65.43 | 1.426 | 2.46 | 2 | 1.230 | 0.780 |
| 24 | 026 | 68.05 | 1.377 | 5.38 | 5 | 1.076 | 0.645 |
| 25 | 108 | 68.72 | 1.366 | 15.54 | 13 | 1.195 | 0.717 |
| 26 | 009 | 72.73 | 1.300 | 1.85 | 1 | 1.850 | 1.109 |
| 27 | 030 | 72.92 | 1.297 | 1.92 | 1 | 1.920 | 1.151 |

**Table 2.** Comparison of Texture Coefficients for Various planes of Superconducting Samples P2, P3 and P4.

| Sr. No. | hkl | Texture Coefficients (T.C.) | | |
|---|---|---|---|---|
| | | P2 | P3 | P4 |
| 1 | 003 | 2.597 | 2.082 | 0.924 |
| 2 | 004 | 2.303 | 1.417 | 1.365 |
| 3 | 005 | 2.946 | 2.223 | 1.009 |
| 4 | 006 | 2.684 | 1.761 | 0.925 |
| 5 | 007 | 3.179 | 2.259 | 1.187 |

Temperature dependent resistivity measurements for samples P2, P3 and P4 are given in Figure 5 indicating that they are superconducting above 86 K. Sample P1 does not superconduct above 78 K. All four samples show metallic behaviour above $T_c$ and superconducting samples have sharp transitions around the transition temperature.

Susceptibility measurements on superconducting samples (P2-P4) show single phase behaviour and almost the same sharp transition temperature as observed by RT-measurements. Such a temperature at 87 K curve is given in Figure 6 for sample P3 which also indicates sharp transition.

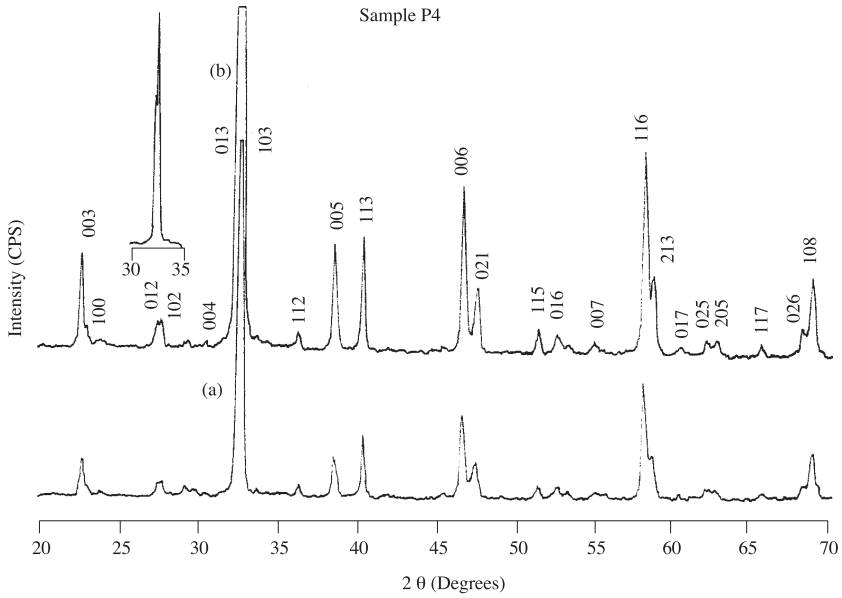



**Figure 4.** XRD patterns of sample P4: a. after 3rd heating b. after last heating

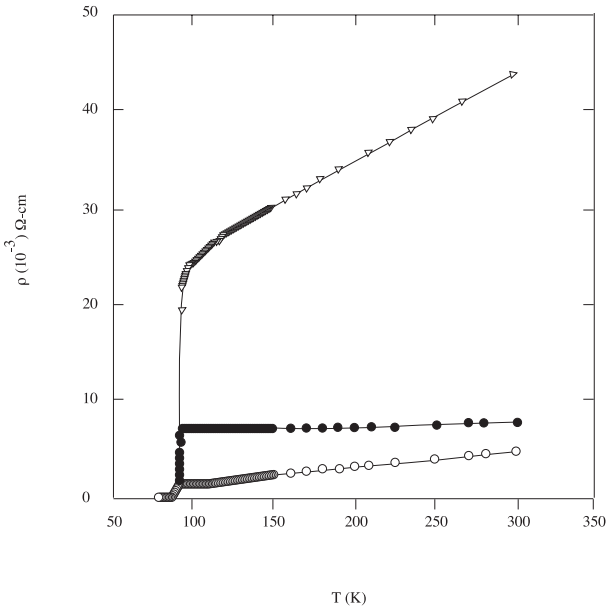



**Figure 5.** Temperature dependence of Resistivity of samples P2, P3 and P4: Δ Sample P2 ○ Sample P3 ● Sample P4

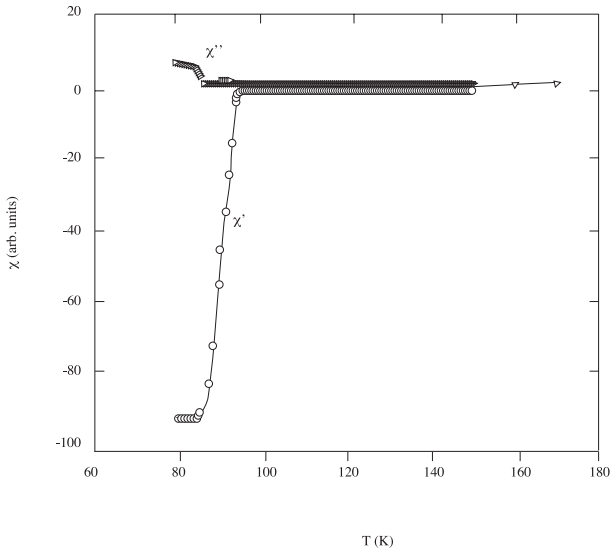
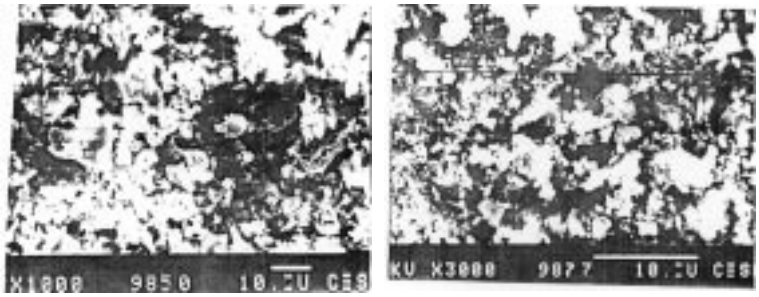



**Figure 6.** Susceptibility measurements for sample P3.

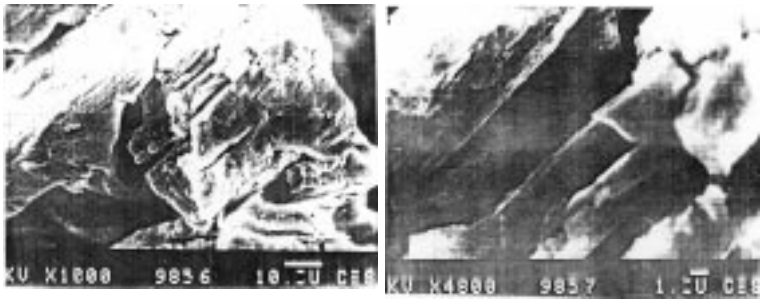
Scanning electron micrographs of tetragonal samples P1-P4 are shown in Figures 7-10. The grains of tetragonal P1 (Figure 7) are irregular and their size covers a wide range

from (0.5-5.0 $\mu$ m). Figure 7 shows that the material is highly porous (dark areas) and the grains are not oriented in any particular direction.



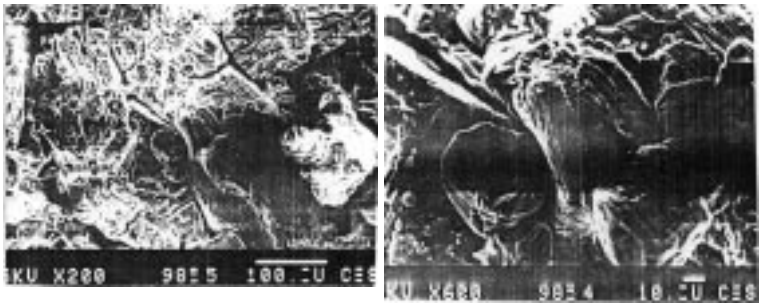
(a) (b)

**Figure 7.** Scanning electron micrographs of sample P1.



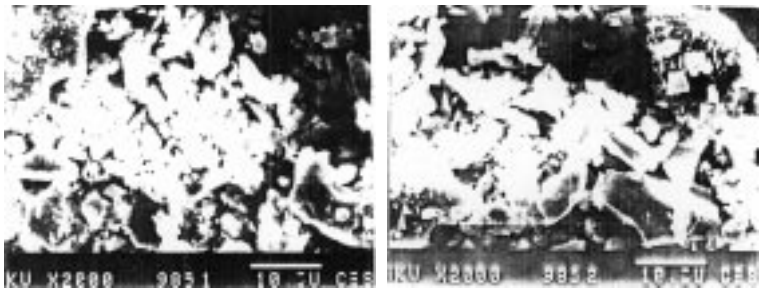
(a) (b)

**Figure 8.** Scanning electron micrographs of sample P2.



(a) (b)

**Figure 9.** Scanning electron micrographs of sample P3.



(a) (b)

**Figure 10.** Scanning electron micrographs of sample P4.

Scanning electron micrographs of samples P2 and P3 are shown in Figures 8 and 9, taken at different magnifications. The micrographs reveal almost a totally different morphology of the grains compared to that of sample P1. Instead of very small sized irregular grains, a highly textured, large sized ($> 40\mu m$) rod-like grains having large contact area between them are seen in these micrographs. The micrographs in Figure 9 also through some light on the crystal growth mechanism. In the middle of the micrographs in Figure 9 a nucleus for spiral growth of crystal can be seen. The nucleus grains itself show a layered structure typical of $YBa_2Cu_3O_{7-\delta}$. SEM graphs of sample P4 as in Figure 10 show relatively small sized grains as compared to that of samples P2 and P3. The grains have not grown into large size plate-like structures. Instead, they have very small contact area between themselves and the material have high porosity indicating poor current percolation paths.

From the above SEM results it can be concluded that highly textured large sized plate like grains of superconductor $YBa_2Cu_3O_{7-\delta}$ can be grown if heated between a thermal gradient of 935-945 °C. Heating above and below this temperature range does not produce textured large sized plate-like structure of $YBa_2Cu_3O_{7-\delta}$ superconductor.

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