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Resistance and XRD Measurements of Bi(Pb)SrCaCuO Superconductor

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Abstract

Three superconducting samples with the composition $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ were prepared using solid state technique. The Bi_2O_3, PbO, $SrCO_3$ and CuO powders of 99.99% purity were used as starting raw materials. The powders sample were mixed with the nominal cation ratio Bi:Pb:Sr:Ca:Cu = 0.8:0.2:1:1:1.5. After mixing appropriate quantities, the sample were well prepared by dry grinding. Then the powder was divided into three sets and with the labels Sample 1, Sample 2 and Sample 3. Then the samples were calcinated at constant temperature of 820^{0}C and the pallets of diameter 14 mm and of thickness 1-2 mm were prepared under the pressure of 200 kg/cm^2, 300 kg/cm^2 and 250 kg/cm^2. After that the pallets were subjected to preliminary sintering at constant temperature in the furnace and allowed to furnace cooling to room temperature in air.

The resistance measurements at low temperatures were performed on these samples using a resistivity probe. The sample 1 shows the onset superconducting transition temperature T_{onset} at 101 K and the sample 2 shows the onset superconducting transition temperature T_{onset} at 112 K. The sample 3 shows the onset superconducting transition temperature T_{onset} at 110 K. The XRD measurements also showed the presence of Bi2223 phase in sample 1, the presence of Bi2212 and the Bi2223 phases in the sample 2 and the Bi2223 phase in the sample 3.

***Keywods**: hysteresis loop, solid state technique, superconductor, transition temperature*

INTRODUCTION

Superconductivity is a phenomenon occurring in certain materials at low temperatures, characterized by the complete absence of electrical resistance and the damping of the interior magnetic field.

Superconductivity was first discovered in 1911 by the Dutch physicist, Heike Kammerlingh Onnes[1]. He began to investigate the electrical properties of metals in extremely cold temperatures. It had been known for many years that the resistivity of metals fell when cooled below room temperature, but it was not known what limiting value the resistance would approach, if the temperature were reduced to very close to 0 K. Some scientists, such as William Kelvin, believed that electrons flowing through a conductor would come to a complete halt as the temperature approached absolute zero. Other scientists, including Onnes, felt that a cold wire's resistance would dissipate. Onnes passed a current through a very pure mercury wire and measured its resistance as he steadily lowered the temperature. At 4.2 K the resistance suddenly vanished. Current was flowing through the mercury wire and nothing was stopping it, the resistance was zero. So he suggested that the new state of mercury is known as superconductive state. Kamerlingh Onnes called this newly discovered state, Superconductivity [2].

In 1986, Georg Bednorz and Alex Müller, working at IBM in Zurich Switzerland, were experimenting with a particular class of metal oxide ceramics called perovskites. Bednorz and Müller surveyed hundreds of different oxide compounds [3]. Working with ceramics of lanthanum, barium, copper, and oxygen with composition $LeBaCuO_4$ they found indications of superconductivity at 35 K. Soon researchers from around the world were working with the new types of superconductors. In February of 1987, a perovskite ceramic material with composition $YBa_2Cu_3O_7$ was found to superconduct at 90 K. This discovery was very significant because now it became possible to use liquid nitrogen as a coolant. Because these materials superconduct at significantly higher temperatures they are referred to as High Temperature Superconductors. Since then scientists have experimented with many different forms of perovskites producing compounds that superconduct at temperatures over 130 K. Soon after a superconductor with composition BiSrCaCuO family of ceramic superconductors was discovered [4]. This new class of materials is unique among high temperature superconductors because it does not contain a rare-earth cation, and several compositions within this material system exhibit superconductivity. The superconductors within this family have the general formula $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$, where n = 1 to 3 and indicates the number of CuO layers in the crystal structure. The highest T_c phase has three CuO layers and exhibits a superconductive transition at 110 K. Similarly, the 2212 phase has two CuO layers and the 2201 phase has a single copper oxide plane. These latter two compositions exhibit superconductive transition temperatures of 60-85 K and 20 K respectively [5].

Since the initial discovery of superconductivity in BiSrCaCuO ceramics, the preparation of single phase 2223 materials has proven difficult because the 2212 phase is thermodynamically more favorable at elevated temperatures than the 2223 phase [6-7]. The partial substitution of PbO for Bi_2O_3 has since beenfound to help stabilize the high T_c composition, thereby increasing the volume fraction of this phase [8]. By stabilizing the high T_c phase in BiSrCaCuO ceramics, higher process yields have become possible for products utilizing these compositions.

The resistance or resistivity variation with temperature is one of the main experimental methods for observing superconductivity. Normal state (above T_c) resistivity behavior as well as the transition onset, transition width, and observable zero resistance are important parameters in the characterization of superconducting samples. However, for cases where superconductivity does not exist in a bulk form, the nature of the R-T curve may differ from the expected R-T curve, even though there can be fractions of superconductive phases present, in matrix of non superconducting bulk. On the other hand, non-superconducting layers may mask superconducting grains or regions or grain boundaries, giving rise to different R-T behavior or even non-superconducting behavior. Therefore, the absence of zero resistivity does not rule out the possibility that the sample concerned is not a superconductor. In such doubtful causes, a contact less method, such as magnetic susceptibility or dc magnetization could be employed for further investigations.

RESEARCH METHODOLOGY

Superconducting Sample Preparation Techniques

Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ and CuO powders of purity better than 99.99 % were used as starting raw materials. The powders were mixed with the nominal cation ratio Bi:Pb:Sr:Ca:Cu is 0.8:0.2:1:1:1.5. After thoroughly mixing appropriate quantities, the mixture was grinded to a fine powder.

The grinded powder sample was divided into three portions and kept in ceramic crucibles with the labels as Sample 1, Sample 2 and Sample 3. Then the Samples were fired at constant temperature of 820^0 C, the Sample 1 and the Sample 3 were in the furnace for 24 hours and the Sample 2 for 12 hours. Then the fired powder was again reground.

After that, Pellets of diameter 14 mm and thickness 1-2 mm were prepared under the pressure of 200 kg/cm^2 from Sample 1, under the pressure of 300 kg/cm^2 and from Sample 2 and under the pressure of 250 kg/cm^2 from Sample 3. First set of pellets (Sample 1) were subjected to a preliminary sintering at constant temperature of 860^0 C in the furnace for 60 hours and was allowed to furnace cooling to room temperature in air [9-10].

Second set of pellets (Sample 2) were subjected to a preliminary sintering at constant temperature of 830° C in the furnace for 60 hours and were allowed to furnace cooling to room temperature in air. Then the pellets were reground and palletized under the pressure of 300 kg/cm^2. After that, the pellets were subjected to second sintering at 860° C in the furnace for 60 hours and were allowed to furnace cooling to room temperature in air [9-10].

Similarly, the third set of pellets (Sample 3) were subjected to a preliminary sintering at constant temperature of 820° C in the furnace for 24 hours and was allowed to furnace cooling to room temperature in air. Then the pellets were reground and pelletized under the pressure of 250 kg/cm^2. The above steps were repeated again and the pellets were subjected to final sintering at 860° C in the furnace for 100 hours and were allowed to furnace cooling to room temperature in air [9-10].

X – Ray Diffraction Analysis and Resistance Measurements

Resistivity of the pellets was measured in a closed cycle refrigerator, using the four probe technique. The sample currents used were in the range of 1 – 5 mA. The sample temperature was measured in the temperature range 77 K – 170 K using Ph-Fe resistance thermometer. The liquid nitrogen was used as coolant. While the sample was warmed by electrical heating the resistance of the sample and the corresponding temperatures were recorded. X-ray powder diffraction measurements were also performed using a Shimadzu model XD-7A X-ray diffractrometer.

RESULTS

The resistance measurements and XRD measurements on the sample 1 ($Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$) is presented in Figure 1.

The graph shown at the upper right corner of the figure 1 obtained for the sample 1 exhibits $T_{c,onset}$ temperature of approximately 101 K. This sample showed zero resistance 81 K. The superconducting transition width of the sample ΔT_c were found to be 20 K. It is clear that this sample shows considerably broad superconducting transition and this may be due to the presence of more than one phase or impurities in the sample.

An X-ray diffraction data of the sample 1 showed in the data in figure 1 confirms the existence of the high-Tc phase. The data from the diffraction scan show strong diffraction peaks at $2\theta = 5.803°, 23.199°, 27.603°, 31.122°$ and $33.301°$, and have d values 15.2188, 3.8310, 3.2289, 2.8713 and 2.6883 respectively. The presence of this peak may be due to the

2212 phase and the larger peaks represent the 2223 high-Tc phase of the Bi base superconductor [11]. Furthermore, the diffraction pattern shows a good agreement with the resistance data presented in the upper right corner of the Figure 1.

The resistance measurements and XRD measurements on the sample 2 ($Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$) is presented in Figure 2.

It is apparent that the sample 2 possess $T_{c,onset}$ temperature of approximately 112 K. This sample reaches zero resistance at 81 K as shown in the upper right corner of the Figure 2. The superconducting transition widths of the sample ΔT_c was found to be is 30 K. This sample also shows a broad superconducting transition ΔT_c and this may be due to the presence of more than one phase or impurities in the sample.

X-ray diffraction data of the sample 2 presented in Figure 2 confirms the existence of the higher and lower-Tc peaks. The diffraction data display a small peak at $2\theta = 3.089°$ has d value 28.5747, accompanies the larger peaks at $2\theta = 5.803°$, 27.578°, 31.117° and 33.288° and shows d values 15.2167, 3.2317, 2.8718 and 2.6893 respectively. The peak at $2\theta = 3.089°$ is relatively small compared to the adjacent peak at $2\theta = 5.803°$. The presence of this peak may be due to the 2212 phase and the larger peaks represent the 2223 high-Tc phase of the Bi base superconductor [11].

The resistance measurements and XRD measurements on the sample 3 ($Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$) is presented in Figure 3.

As shown in the upper right corner of the Figure 3, this sample shows a sharp drop in its superconducting transition. The sample exhibits $T_{c,onset}$ temperatures of approximately 110 K. This sample reached $T_{c,zero}$ resistance at 82 K as shown in Figure 3. The superconducting transition widths of the sample ΔT_c was found to be at 26 K.

The sharp drop in the superconducting transition indicates that only one superconducting phase Bi 2223 exists in the sample. An X-ray diffraction measurement of the sample 3 showed in the data in Figure 3 confirms the existence of the high-Tc phase. The diffraction data show strong diffraction peaks at $2\theta = 24.886°$, 27.497°, 31.024°, and 33.197° and 33.197°, and have d values 3.5749, 3.2411, 2.8802, and 2.6965 respectively. The presence of these intense peaks strongly indicates the presence of 2223 high-Tc phase in the sample 3 [11]. Furthermore, the diffraction pattern shown in Figure 3 is in accordance with the resistance data presented for this sample.

DISCUSSION

To study the phases existing in the samples we have to do further analysis. In the Bi-compounds it often occurs that the diamagnetic signal is quite large though the X-ray powder patterns do not show the corresponding superconducting phase. Also a small 'tail' was observed in the resistance curve of sample 2 shown in the Figure 3 and this 'tail' observed at approximately Tc= 101K may not be due to the mixing of the other phases, but due to the extremely porous nature of the sintered samples [9]. Thus regrinding, repressing, and resintering of the sintered pellets were necessary to improve the quality of the samples. It was observed that after the additional treatments, the 'tail' disappears as well as the transition becoming sharper and normal state resistivity reduces. We can clearly see these changes from the Figures 1 and 3. The reason for the observed change may be explained as follows. In as-sintered samples, the poly-crystalline grains are coupled both in the normal state and in the superconducting state because of the volume expansion during the initial sintering process, even ground well. Thus the regrinding and resintering improves the intergrain coupling drastically.

Also one should note that, in these data even the X-ray diffraction pattern shows that one phase is dominant, the resistance vs temperature curves still show the existence of other phases. That is, there is no clear relationship between the percentage of 110 K phase observed in the X-ray diffraction pattern and Tc. This lack of consistency in our observations could be due to the in-homogenities in the distribution of the 110 K phase in the bulk pellets, which lead to preferential percolation during the resistance measurements [10].

It is now well known that an additional process is necessary for the preparation of good 2223 samples. Introduction of Pb and long time sintering under low oxygen pressure remarkably improves the quality of the 2223 samples [12]. The high onset and critical temperatures can only be obtained by replacing the Bi with Pb atoms in the nominal composition. The improvement of the characteristics at higher temperatures in the Bi compound when Pb is added must be related to a different type of physical process which may be associated with changes in the kinetics of the solid state reaction, which is believed to speed up the formation of this 2223 phase.

The XRD patterns of the samples taken with the same X-ray intensity setting are shown in Figures 1, 2 and 3. From differences between these XRD patterns we can conclude that, the impurities, organic compounds and CO_2 were removed from the superconducting sample. This can be attributed to incomplete reaction products, which are non-superconducting. But in sample 3 the sintering temperature and time were higher than the sample 1 and

sample 2. So that the sample 3 produces a good onset superconducting transition temperature and also the sample exhibits a 2223 superconducting phase.

It is well known that the lack of long-range order or smallness of crystal grains usually broadens the XRD peaks. The diffuse nature of the XRD peaks of the samples prepared by the double-sintering process could therefore, be associated with the microstructure of the grains, which may have acquired a glassy or amorphous nature, during the growth process, as a result of the two-stage sintering process.

The main limitation to the formation of long length of BSCCO conductors with good Jc performance, are phase purity, microstructural inhomogeneities and large scale imperfections such as cracking and voiding. Understanding and control of the phase chemistry is essential in order to obtain reproducible properties. We have determined phase equilibria in the Bi-2212 system and phase stability of (Bi,Pb)-2212 and (Bi,Pb)-2223 as a function of temperature and reduced oxygen partial pressures. This information has allowed alternative precursor phase combinations and processing routes to be explored.

CONCLUSION

Sample	Transition Temperatures (onset) K	X-Ray Diffractions peaks at 2θ
1	101	5.803°, 23.199°, 27.603°, 31.122° and 33.301°.
2	112	5.803°, 27.578°, 31.117° and 33.288°
3	110	24.886°, 27.497°, 31.024°, and 3.197°.

Table 1: The Onset Transition Temperature and X-Ray Diffractions peaks for sample 1, 2 and 3

Sample 1 and Sample 2 show broad transitions which may be due to the existence of Bi2212 and Bi2223 superconducting phase whereas sample 3 shows single drop conforming the existence of Bi2223 superconducting phase.

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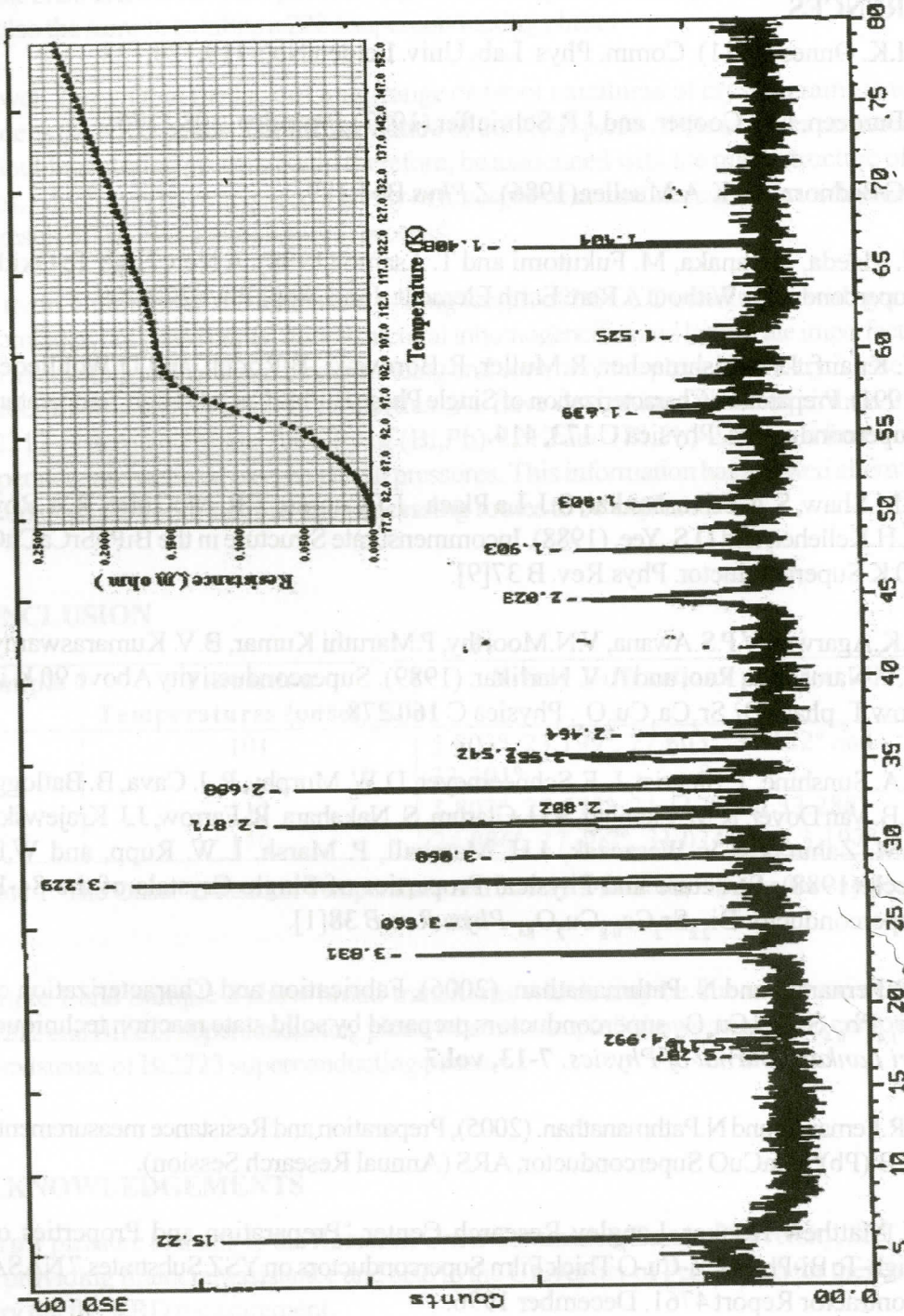

Figure 1: The X – Ray diffraction pattern and resistance measurement of the fully reacted sample 1. Intensity peak of Bi2223 phase and the superconducting transition temperature T_{onset} at 101 K are indicated.

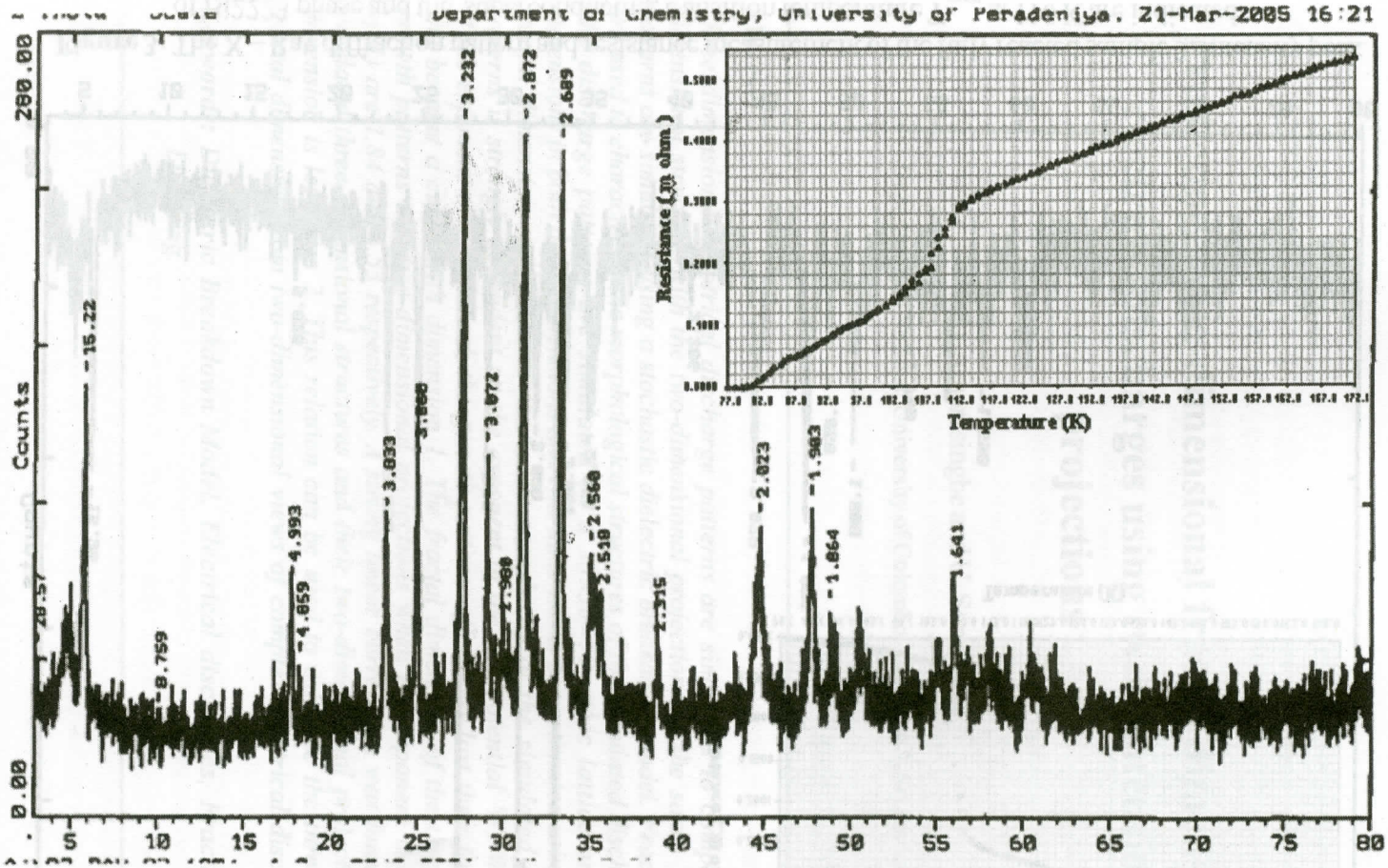

Figure 2: The X – Ray diffraction pattern and resistance measurement of the fully reacted sample 2. Intensity peak of Bi 2212 or Bi2223 phase and the superconducting transition temperature T_{onset} at 112 K are indicated.

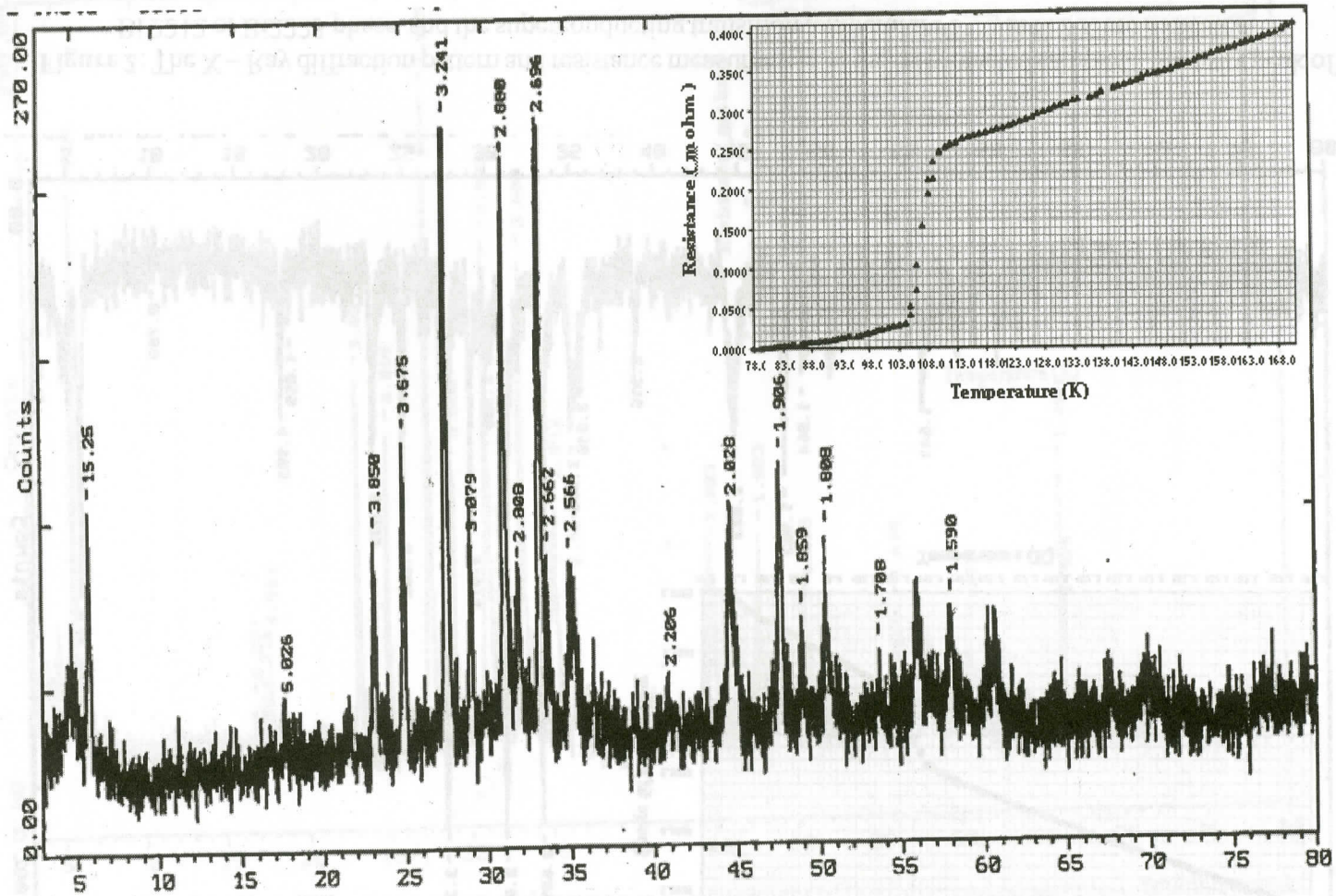

Figure 3: The X – Ray diffraction pattern and resistance measurement of the fully reacted sample 3. Intensity peak of Bi2223 phase and the superconducting transition temperature T_{onset} at 110 K are indicated.