

Preparation and Characterization of Hot-Pressed and Sintered BiPbSrCaCuO Superconductor

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ABSTRACT

Powder compacts of the system $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ with $0 \leq x \leq 0.5$ molar ratio using both techniques; isothermal hot pressing and the solid state reaction (sintering). The XRD of the hot pressed powder compacts of the nominal compositions $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ showed 2212 and 2223 phases. The resistivity temperature variations belonging to the composition $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ showed metal-superconducting transition at $T_{\text{ons}} = 143$ K for the annealed sample for 24 h. The annealed nominal composition $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ for 18 h showed metal to superconducting transition at 80 K.

Keywords: Electrical Resistivity; Superconductors; Hot Pressing; Sintering

1. Introduction

Podder *et al.* [1] have prepared the nominal compositions $\text{Bi}_{1.7}\text{Pb}_{0.25}\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_y$ and $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_y$ using the conventional solid-state reaction method. PARK and IM [2] have prepared the system $\text{Bi}_{0.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_{1.8}\text{O}_y$. The sol-gel method was used for preparation of high T_c phase in the Bi-Pb-Sr-Ca-O system [3,4]. Accordingly [5], the 110 K single phase in Pb-doped Bi-Sr-Ca-Cu-O system was prepared by the method of co-decomposition of nitrates. Pellets of the composition $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_{10}$, which was reported as the optimum composition for obtaining pure high T_c phase in the Bi-Pb-Sr-Ca-Cu-O system were prepared by thoroughly mixing Bi_2O_3 , PbO , SrCO_3 , CaCO_3 and CuO [6]. Calcination and sintering with intermediate regrinding several times have been described [6]. Kanai *et al.* [7] used commercial powders of 3N pure Bi_2O_3 , PbO , SrO , CaO and CuO_y and have obtained the 2212 phase with a small amount of the 2201 phase. Kawahara *et al.* [8,9] prepared the high T_c superconductors $(\text{Bi}, \text{Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ by solid state reaction and obtained the high T_c 2223. Bulk superconductors of $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{1.91}\text{Ca}_{2.03}\text{Cu}_2\text{O}_{3.06}$ were prepared by hot-pressing sintering [10]. Noudem *et al.* [11,12] have optimized a texturing process of Bi-Pb-Sr-Cu-O (2223) superconducting ceramics by hot pressing. The Pb solubility of the 2212 and 2223 phases has been tested by Peter Majewski *et al.* [13]. Lidija *et al.* [14] demonstrated the ability of aerosol synthesis of multicomponent Bi-based

high T_c superconducting particles from pure nitrate solutions with improved compositional homogeneity all over the powder. Spherical solid Bi-Sr-Ca-O rich particles with the mean particle size around 400 nm were obtained from common nitrate solutions [14]. Glass-ceramic technology found to be a good method of obtaining BiSrCaCuO superconductors [15], especially $(\text{Bi}, \text{Pb})_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ phase forms well by this method.

Best superconducting properties found to be achieved at the temperature of annealing about $840^\circ\text{C} - 850^\circ\text{C}$ [15]. Millera *et al.* [16] found that oxide $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{CuO}_x$ and $(\text{Bi}_{0.8}, \text{Pb}_{0.2})_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ glasses, annealed above 470°C , crystallize. The crystalline phases forming during annealing were, among others, oxide superconductors: $(\text{Bi}, \text{Pb})_2\text{Sr}_2\text{Cu}_3\text{O}_x$ (2201 with $T_c = 10$ K), $(\text{Bi}, \text{Pb})_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (2212, T_c 85 K), and $(\text{Bi}, \text{Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (2223, T_c 105 K). The composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ was prepared, the super conducting transition temperatures found to be 103 K, 111 K and 110 K depending on the condition of preparation [17]. Bi(Pb)-Sr-Ca-Cu-O thin films have been prepared using Nd-YAG pulsed laser ablation on Mg substrate [18], it was found that increasing of the annealing temperature to 870°C and 880°C led to increasing the intensity of T_c phase and the appearance of semiconducting phase.

2. Experimental Technique

Using bismuth oxide, strontium oxide, lead oxide and

copper oxide of 99.99 purity have been used to prepare powder compacts of the system $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ with $0 \leq x \leq 0.5$ molar ratio using both techniques; isothermal hot-pressing and the solid state reaction (sintering). Appropriate weights of the route compounds satisfying a certain nominal composition were determined to the fourth decimal using an electrical analytical balance type (Fisher scientific XA 2000 DS) with sensitivity better than 10^{-4} gm. The pre-determined weight of the route compounds Bi_2O_3 , PbO , SrO , CuO and CaO_3 were mixed together in molar ratios $2 - x:x:2:2:3$ which are convenient to satisfy preparation of nominal compositions of the system $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ with $x = 0.1, 0.2, 0.3, 0.4$ and 0.5 . The method used for preparation of batches of powders was essentially based on that described previously elsewhere. The mixtures were dissolved in equivalent amount of Conc. HNO_3 . The solution was stirred and heated at 600°C , until it becomes dry to form a precipitate with blue color. The blue product was then heated at 820°C for 24 h, and then left to cool to room temperature, after that it was grinded and heated again at 820°C for another 24 h, and then left to cool to room temperature. The product was then grinded thoroughly. Each of the five batches are corresponding to five different nominal compositions was divided into three parts. One part was used for preparing powder compacts by using hot-pressing technique. In this case, a pre-determined weight of the powder of the desired batches was directly charged into the die of the hot-pressing technique. Then it was isothermally hot-pressed at the temperature $845^\circ\text{C} - 850^\circ\text{C}$ for 12 h under evacuation better than 10^{-3} torr, and under application of the uni-directional pressure of 5 ton/cm^2 . The outcoming compacts were cooled down to room temperature by shutting down the power of the furnace. The prepared tablets are clean and parallel and optically flat.

The x-ray diffraction examinations were carried out using Schemadzu x-ray diffractometer with $\text{CuK}\alpha$ target.

The surface microstructure of the specimens were examined by means of a scanning electron microscope type Jeol JsM-5300 (Japan), where coating with an evaporated thin film of gold of 100 \AA thickness has been carried out to avoid building up of surface charges and reduce damage which might result from heating due to the incident electron beam.

The melting temperature, crystallization temperature and the transition width were studied using Shimadzu differential thermal analyzer system-50 with heating rate $10^\circ\text{C} \cdot \text{min}^{-1}$.

The d.c electrical resistance of the prepared compacts was measured by means of the slandered four-terminal electrical resistivity method using a d.c stabilized power supply type F B impo, Gould Advance Beta digital multimeter, Keithely electrometer type 610 C and d.c stabi-

lized power supply type IRWIN.H.T power supply E.J134. The environmental temperature was monitored using copper-constantan thermocouple.

3. Results & Discussions

3.1. XRD Analysis

For only hot-pressed powder compact of the nominal composition $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$, the XRD proved that the most intense and the fourth intense phases could be identified as 2212 as shown in **Figure 1(a)**. The second and fifth intense phases were also the same and could be identified as the high T_c phase 2223. Two peaks with equal intensities, one is corresponding to the phase 2223 and the other is corresponding to the phase $2223 + 2212$ were appeared with appreciable intensity at $d = 2.7 \text{ \AA}$ and 3.075 \AA , both represent together the third intense phase. The phase $\text{Bi}_2\text{Sr}_3\text{Cu}_2\text{O}_y$ could be observed. The nonsuperconducting phases $(\text{Sr}, \text{Ca})\text{CuO}_2$ could be identified and represents the less intense one on the diffractogram.

For the nominal composition $\text{Bi}_{1.9}\text{Pb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_y$, the XRD shown in **Figure 1(b)** proving that the most intense, the second and the fifth intense phases are the same and could be identified as $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_x$, the third intense phase was 2212 and the fourth intense one was 2223. Two unknown phases seemed existed and the non-superconducting phase $(\text{Sr}, \text{Ca})\text{CuO}_2$ could be identified with appreciable intensity.

For the nominal composition $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_y$, the XRD shown in **Figure 1(c)** proving that the most intense, the fourth and the fifth intense phases were the same and could be identified as $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_x$. The second intense phase could be identified as 2223 and the third one was 2212. Only one phase could not be identified. The nonsuperconducting phase SrCuO_2 and CaCuO_2 was entirely disappeared.

The XRD of the only hot-pressed nominal composition $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_y$ shown in **Figure 1(d)**, where the most intense phase 2212 can be identified. Two peaks with equal intensities, one corresponding to the phase 2212 and the second correspond to the phase 2223 could be identified and could be considered as the second intense phase. The third intense phase could be identified as $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_y$. The fourth and the fifth intense phases could be identified respectively as 2212 and 2223. Other non-superconducting phases containing and not containing Pb could be also identified which are namely Ca_2PbO_4 , Ca_2CuO_3 and $(\text{Sr}, \text{Ca})\text{O}_2$ and CaO . Meanwhile, the phases $\text{Bi}_2\text{Sr}_3\text{Cu}_2\text{O}_y$ could be identified with an appreciable intensity.

As it is seen, the most frequent phase was 2223. Besides, the phase 2212 which represents the most intense seemed existed with an appreciable abundance. The less

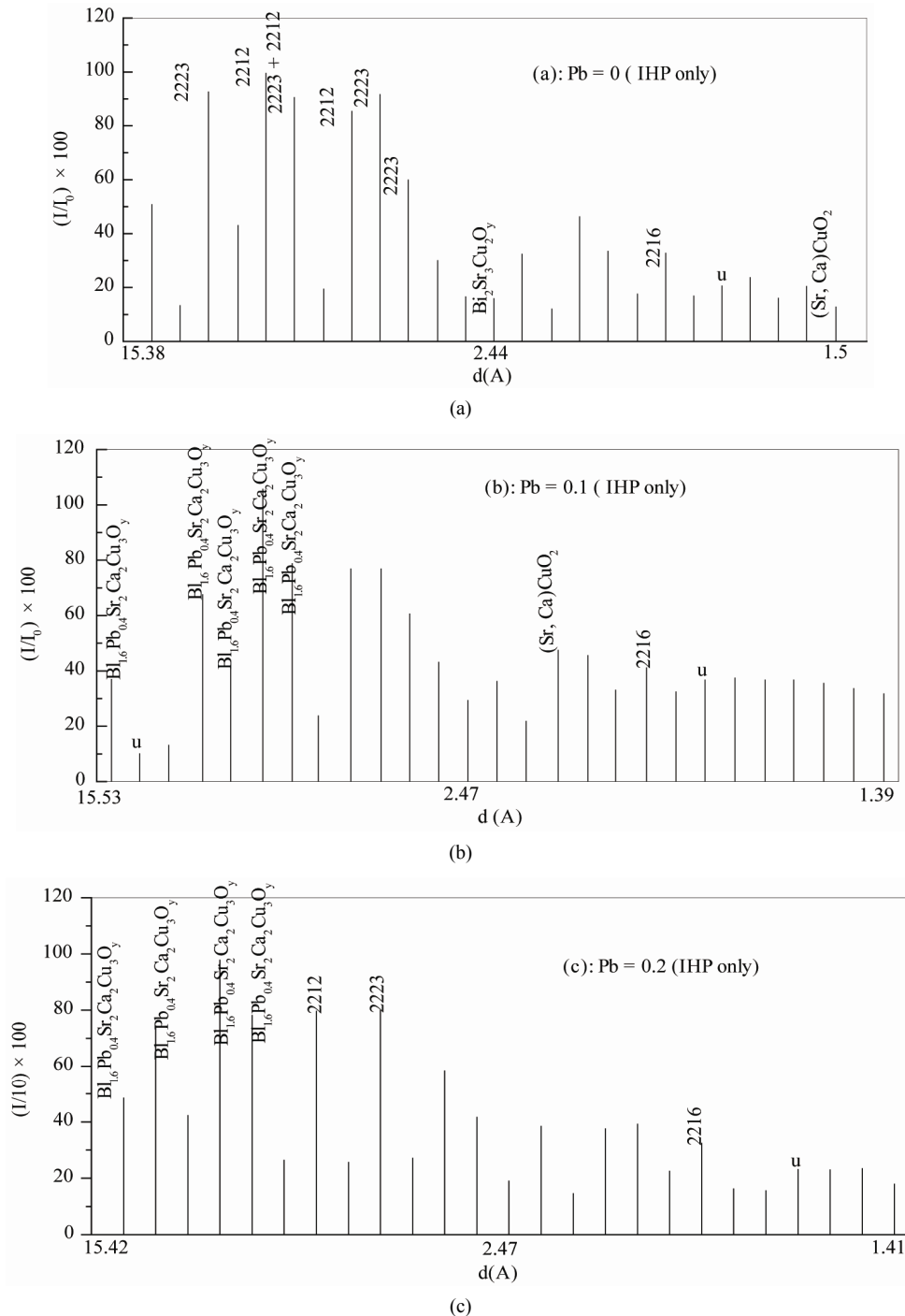
abundance seemed belonging to the phase 2201.

The XRD of the nominal composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_y\text{Ca}_2\text{Cu}_2\text{O}_y$ shown in **Figure 1(e)**, where the most intense phase was the non-superconducting bi-oxide Ca_2CuO_3 . The second and the third intense phases were the same and could be identified as 2234. The fourth and fifth intense phases were 2201 and 2212 respectively. So, it is obvious that the internal microstructure of this compact is quite different from all the

other former ones. Other non-superconducting phases namely SrCO_3 , Ca_2PbO_3 , Ca_2CuO_3 and $(\text{Sr}, \text{Ca})\text{CuO}_2$ with appreciable intensities could be identified.

It can be said that, the most frequent phase was 2223. The non-superconducting phase are also frequent and with appreciable intensities.

The XRD of the last hot-pressed powder compact $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_y$ shown in **Figure 1(f)**, where the most intense phase was the low T_c 2212. The second, the



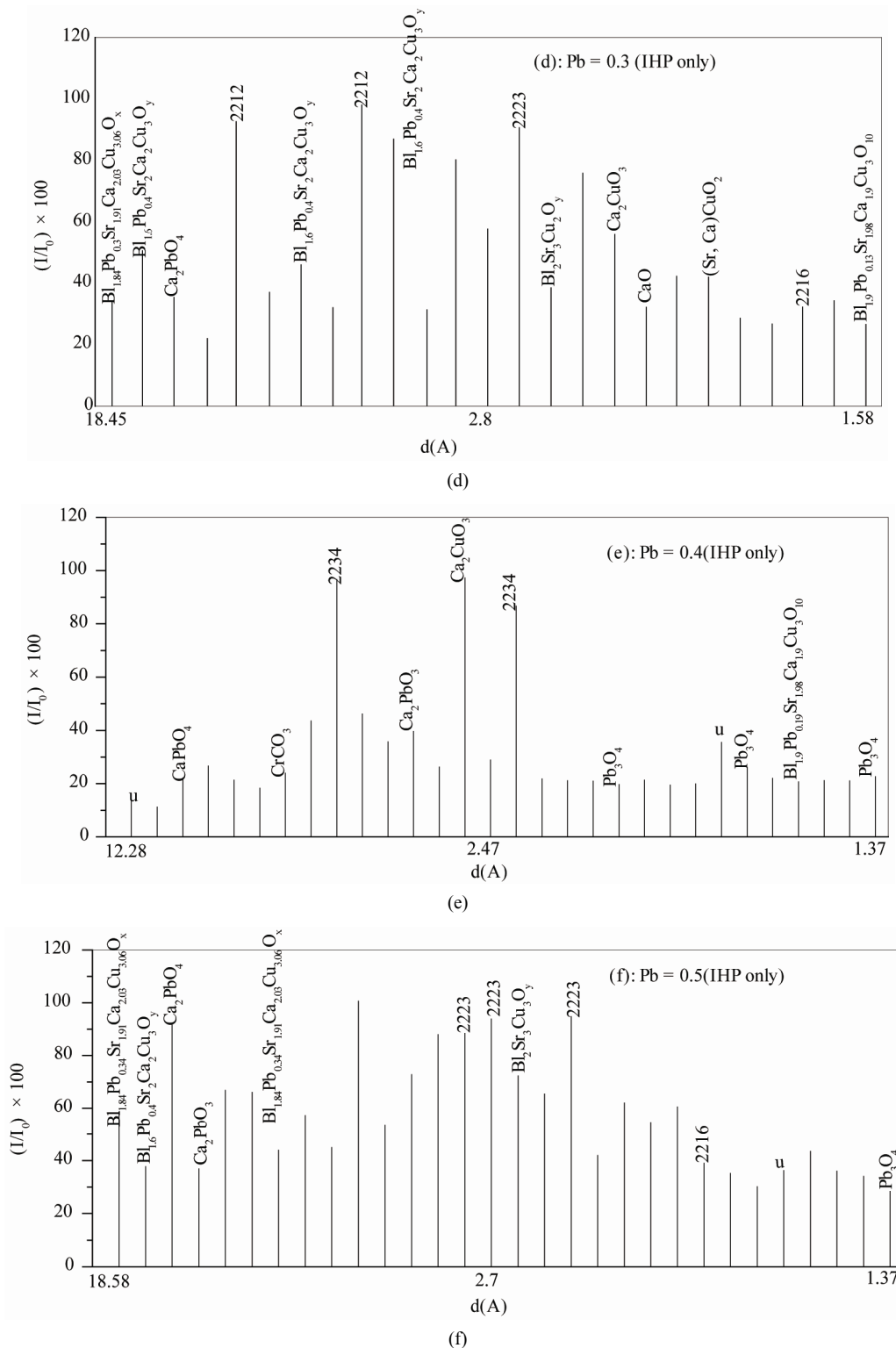


Figure 1. X-Ray diffractograms of IHP powder compacts of the compositions $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$.

third and the fifth intense phases were the same and could be identified as 2223. The fourth intense phase was the non-superconducting bi-oxide Ca_2PbO_4 . The mixed phases 223 + 2212 could be also identified. Also, the

phase $\text{Bi}_2\text{Sr}_3\text{Cu}_2\text{O}_y$ seemed existed with an appreciable intensity. The two phases $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_y$ and $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{1.91}\text{Ca}_{2.03}\text{Cu}_{2.06}\text{O}_y$ could be identified with appreciable intensities. The most frequent phases were

2223 and 2212.

Comparing all the diffractograms on **Figures 1(a-e)**, it is clear that the role of Pb content on the formed phases in the unified condition hot-pressed powder compacts of the system $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ becomes clear. Both kinds and intensities of the phase seem depending strongly on the content of lead in the nominal compositions. Taking into account the three essential phases 223, 2212 and 2201 their maximum intensities changed with the content of Pb in the nominal compositions as shown in **Figure 2**. It is obvious that, both the high T_c 223 and low T_c 2212 phases could be existed in all the considered nominal compositions $0 \leq x \leq 0.5$. The very low T_c phase 2201 could not be identified in nominal compositions containing less than 0.3 Pb. In addition, the maximum intensity of both phases 223 and 2212 changed in similar manner with enriching with Pb over the whole considered molar ratio of Pb.

For isothermally sintered (IS) powder compacts of the nominal compositions of the system $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ then post-annealed (IPA) at 800°C for 30 h, the x-ray diffractograms were as shown in **Figure 2**.

For the nominal composition $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$, the most intense phase was the 2223. The other four successive intense phases were 2212. Two phases were appeared $\text{Bi}_2\text{Sr}_3\text{Cu}_2\text{O}_y$ and $\text{Bi}_2\text{Sr}_2\text{CuO}_6$.

3.2. DTA Analysis

For the as hot-pressed samples of the nominal composi-

tions of the system $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_y$, the DTA thermogram was as shown in **Figure 3** revealing no-exothermic peaks could be detected. Besides, it contained two endothermic peaks with at 430°C and 866.86°C . The low endo-thermic temperature which can be attributed to partial melting increased continuously with enriching with Pb as shown in **Figure 4** where the endothermic peaks were at 796.49°C and 925.46°C respectively.

3.3. Electrical Properties

The temperature dependences of the electrical resistivity of both hot-pressed and post annealed powder compacts are as shown in **Figure 5**.

The as-hot pressed powder compacts behaved similar to normal semiconductors. For 6 h of annealing at 800°C for 30 h, the behavior was still that of semiconductor in the range above 93 K. At $T = 93$ K, semiconductor to semimetal transition occurred and considered as an onset temperature T_{ons} , and the resistivity felled very sharply with decreasing the temperature predicting of attaining the zero-resistance state at $T_c = 77$ K. Prolongating the time of post-annealing to 12 h, the behavior became similar to that of metals over the whole range considered for T. Despite transition to superconducting state did not hold, instead, the extrapolation to 0 K gave value for the residual resistivity 0.02 ohm-cm. More prologation of post-annealing to 18 h resulted in drastic decrease of the compact's resistivity. The extrapolation to 0 K gave value for the residual resistivity 0.012 ohm-cm. At 24 h of

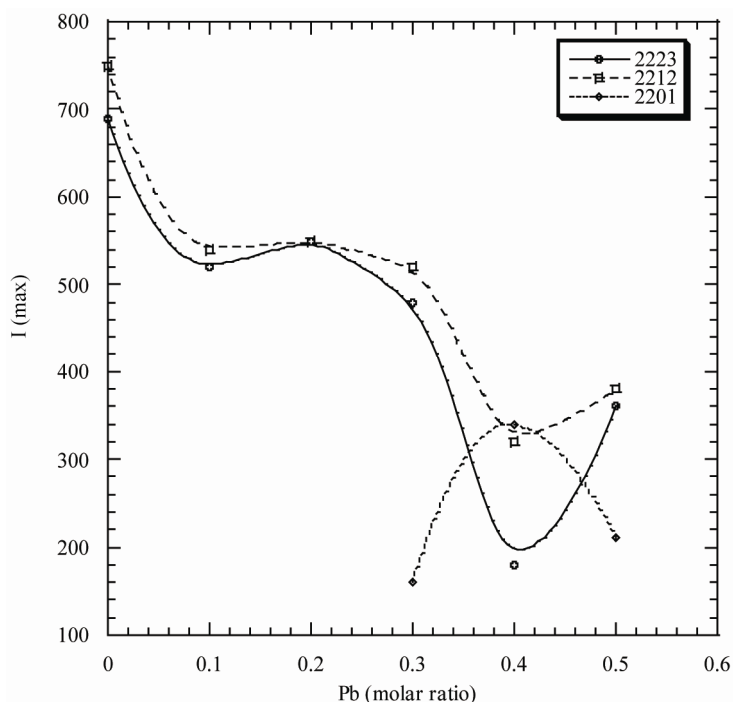


Figure 2. Variations of the maximum intensity of the phases 2223, 2212 and 2201 on the molar ratio of Pb in the only hot-pressed compacts of the nominal compositions of the system $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$.

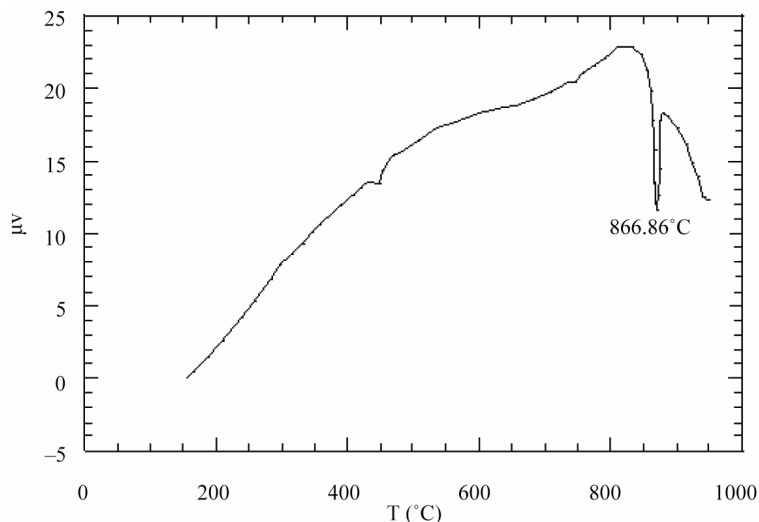


Figure 3. DTA thermogram of only hot-pressed powder compact of the nominal composition $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_y$.

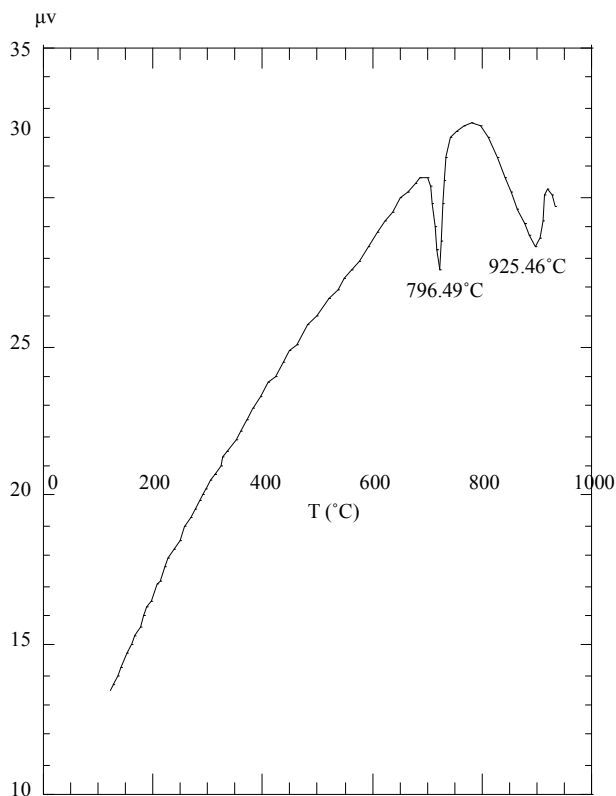


Figure 4. DTA thermogram of only IHP powder compact of the nominal composition $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$.

post-annealing, the resistivity-temperature curve seemed similar to the case 18 h. The extrapolation to 0 K gave value of residual resistivity 0.035 ohm-cm.

From above, it can be said that, the nominal composition $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ is not convenient to attain a single superconducting phase.

Addition of lead forming the composition

$\text{Bi}_{1.9}\text{Pb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ resulted in temperature dependences of resistivity of as-hot pressed and post-annealed powder compacts as shown in Figure 6. The behavior of the as-hot pressed compact was that of semiconductors. Different successive transitions could be observed when post-annealing was carried out for the periods 6 and 12 h. The resistivity decreased continuously with decreasing temperature for longer post-annealing times. Transition to superconducting state could not be held at all. Instead, the extrapolations to 0 K predicted values for the residual resistivity equal to 0.227, 0.2, 0.053, 0.01 and 0.048 ohm-cm.

So, the nominal composition $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ can not result in formation of superconducting phase.

Hot-pressed and post-annealed powder compacts containing 0.2Pb possessed temperature dependences of resistivity as shown in Figure 6.

It is observed that, enriching with Pb to be resulted in a drastic decrease in the values of resistivity of the only hot-pressed compact. At 6 h post-annealing, semiconductor-semimetallic transition occurred at 103 K. The residual resistivity belonging to the annealing times 12, 18, 24 and 30 h are 0.019, 0.004, 0.004 and 0.012 ohm-cm respectively.

From above, hot-pressing and post-annealing of powder compacts of the nominal composition $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ did not result in superconducting transition.

The temperature dependences of the electrical composition belonging to the nominal composition $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ are also comparable to those for the other former compositions. The extrapolations to 0 K of lowest temperature parts of the resistivity temperature curves, gave values for the residual resistivity equal to 0.0155, 0.012, 0.018 and 0.017 ohm-cm for the times 12, 18, 24 and 30 h respectively.

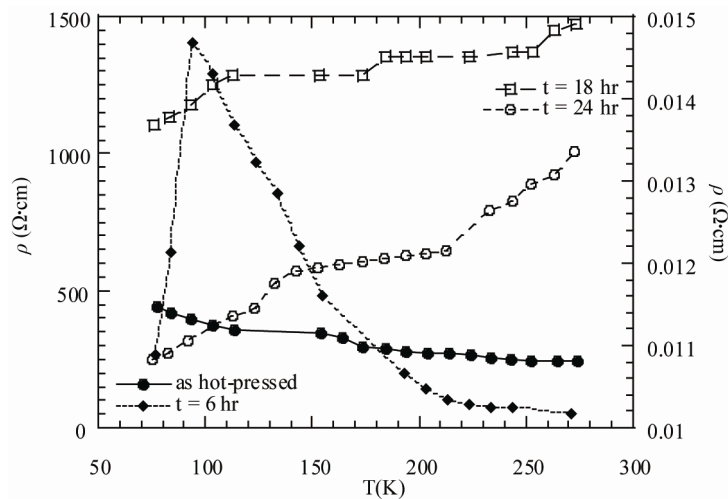


Figure 5. Resistivity-temperature dependence of as-hot-pressed and post-annealed for different times of the powder compacts of the nominal composition $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$.

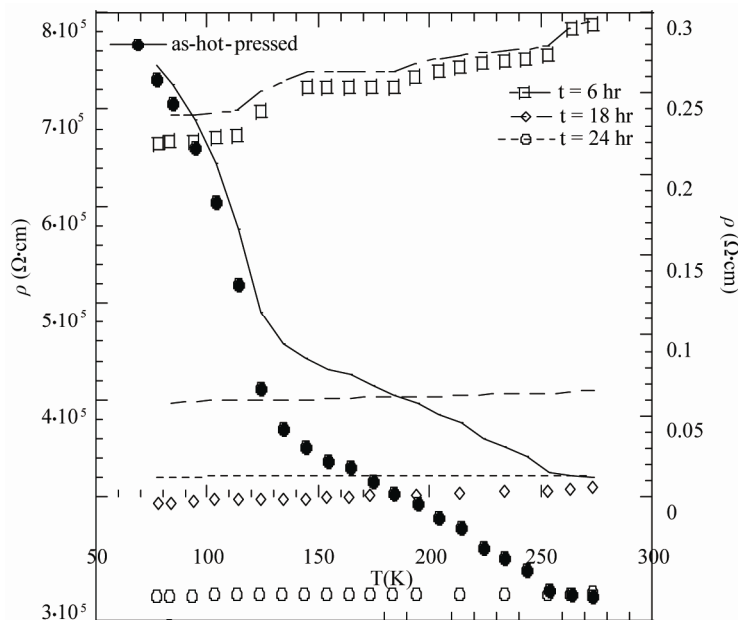


Figure 6. Resistivity-temperature dependence of the as-hot-pressed and post-annealed for different times of powder compacts of the nominal composition $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$.

For the composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$, the resistivity changed with temperature similar to the normal semiconductors.

It is clear that non of the later compacts show superconducting phase.

Figure 7 displays the relationship between the electrical resistivity versus the temperature for the

$\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$. The as-hot-pressed and post annealed for 6 h samples, the resistivity shows semiconductor-semimetallic transition at 124 K. The post-annealed sample for 12 h exhibited semiconducting behavior over the whole range considered for T. Post-annealing for 18,

24 and 30 h resulted in semimetallic behavior over the whole range considered for T. The extrapolation to 0 K predicted values for the residual resistivity equal to 0.01, 0.111, and 0.125 ohm-cm for the times of post annealing 18, 24 and 30 h respectively.

As for the former compositions, addition of Pb can result in modification of the behavior of ρ -T dependence as well as in the values of resistivity.

The $\text{Ln}\rho$ vs $1/T$ relations belonging to the as-hot-pressed and the post annealed samples found to be straight lines verifying the following relation

$$\rho = \rho_0 e^{\Delta E/KT}$$

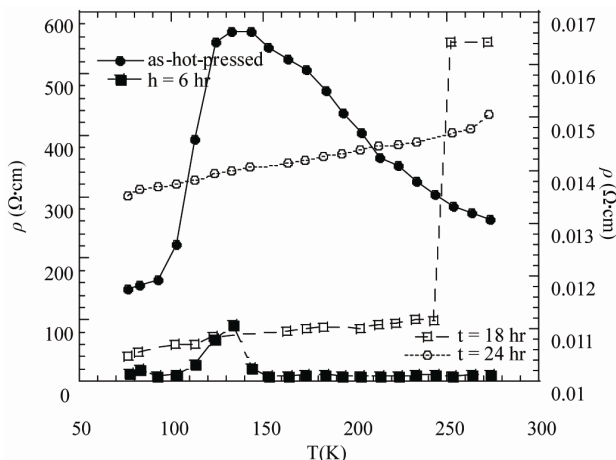


Figure 7. Resistivity-temperature dependence of the as-hot-pressed and post-annealed for different times of powder compacts of the nominal composition $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$.

where ΔE is the activation energy of conduction, ρ_0 is the pre-exponential; k is the Boltzman’s constant. Values of ΔE are calculated and recorded in **Table 1**.

It is obvious that these values of the electrical conduction activation energy are very small with respect to those recorded for normal semiconductors. On the other hand, the values of ΔE decreased with transition from the higher to lower range of T , except for those belonging to the annealed composition $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ for 6 h. Meanwhile, the values of $\Delta E = 0.1579, 0.2152, 0.2377$ EV are comparable with those recorded for the narrow gap semiconductors.

The sintered samples of the nominal composition $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$, shows the temperature dependence of the electrical resistivity for both as-sintered and post-annealed powder compacts which has the behavior of semiconductors. For the shortest period of post-annealing, (6 h), the behavior was similar to that for metals. Prolongating the time of annealing to 24 h results in superconducting transition with onset temperature $T_{\text{ons}} = 113.8$ k and the transition temperature $T_c = 101.7$ k with transition width $\Delta T = 12.1$ k. The reason of such transition may be revealed on referring the data of the microstructural analysis. However, from the first glimpse, it could be speculated that high concentration of the single 2223 or b2212 superconducting phase becomes existed in the compact. Furthermore, when the time of post-annealing was prolonged to 30 h, the compact exhibited also metal to superconducting state transition at almost the same onset temperature as for the former case $T_{\text{ons}} = 110$ k and T_c was almost the same and equal to 100 k with $\Delta T = 10$ k. Except, a tail appeared with $T_1 = 40$ k. This tail may be due to weak link between the grains of superconducting phases also may be due to un-expected intergrowth of non-superconducting phases. Both weak link and intergrowth processes can be regarded as collective reasons of the observed increase in resistivity (an order of magnitude) when the time of post annealing was prolonged from 24 h to 30 h.

Addition of 0.1 Pb on the expense of Bi resulted in resistivity-temperature dependence which did not reveal any superconducting phase transition.

Table 1. Values of the activation energy ΔE for as hot-pressed and post-annealed powder compacts of nominal compositions of the system $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$.

Composition	Time of annealing (h)	ΔE (EV)
$\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$	zero	$9.3 \times 10^{-5}, 4.9 \times 10^{-5}$
	6	$6.04 \times 10^{-4}, 1.3 \times 10^{-4}$
$\text{Bi}_{1.9}\text{Pb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$	zero	$9.06 \times 10^{-3}, 3.07 \times 10^{-3}$
	6	0.1579, 0.0083
$\text{Bi}_{1.8}\text{Pb}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$	zero	0.1579, 0.0083
	6	0.0465, 0.2152
$\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$	zero	0.1095, 0.0132
	6	0.0192
$\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$	zero	0.2377, 0.03269, 0.00406
	6	0.071, 0.030
	12	0.078, 0.038
	18	0.072, 0.025
	24	0.078, 0.024
	30	0.075, 0.030
$\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$	zero	0.0218319
	6	0.003, 0.106
	12	$8.16 \times 10^{-3}, 5.51 \times 10^{-3}, 2.3 \times 10^{-3}$

The ρ -T variation belonging to the composition $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ shows metal-superconducting transition at $T_{\text{ons}} = 143$ k for the annealed sample for 24 h as shown in **Figure 8**. Further, the zero-resistivity state could be attained at a high temperature $T_c = 134$ k with transition width $\Delta T = 8.7$ k. For the longest time considered for post-annealing (30 h), the electrical resistivity reach zero value at $T_c = 79$ k as shown in **Figure 8**.

Enriching with lead of 0.3 and 0.4 Pb did not show any superconducting phase transitions.

The behavior of ρ -T belonging to the nominal composition $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ revealed that annealing for 18 h was accompanied with a metal to superconducting transition at 80 k and the zero-resistivity state reached at $T_c = 73.8$ k.

Values of the activation energies for electrical conduction ΔE_s in the sintered powder compacts of the nominal composition $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ have been obtained from the $\ln\rho-1/T$ plots which found to be straight lines. Values of ΔE_s are recorded in **Table 2**.

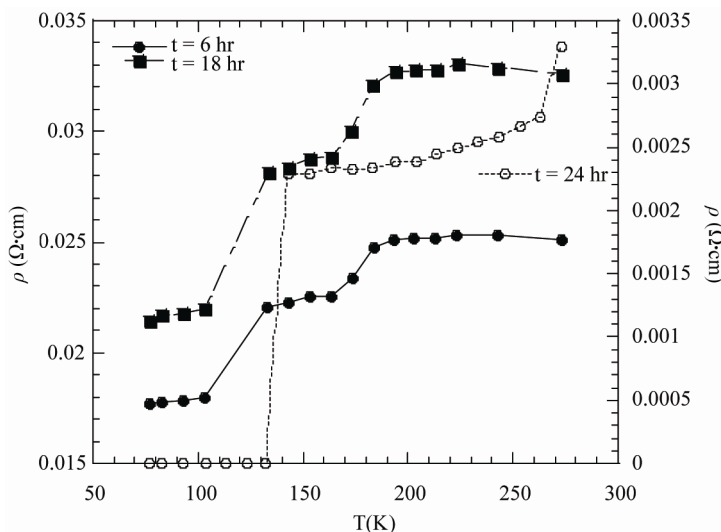


Figure 8. Resistivity-temperature dependence of the as-sintered and post-annealed for different times of powder compacts of the nominal composition $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$.

Table 2. The values of the activation energy ΔE_s of the as-sintered and annealed compacts of the nominal composition of the system $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$.

Composition	Annealing time (h)	ΔE_s
$\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$	Zero	0.009, 0.0005
	12	0.00004
$\text{Bi}_{1.9}\text{Pb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$	12	1.9×10^{-6}
	18	8.1×10^{-7}
$\text{Bi}_{1.8}\text{Pb}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$	Zero	1.1×10^{-4} , 7.8×10^{-6}
	12	1.4×10^{-5}
	18	1.2×10^{-5}
	30	4.5×10^{-6}
$\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$	Zero	5.9×10^{-5} , 5.6×10^{-4} , 3.3×10^{-5} , 1.7×10^{-3} , 5.8×10^{-4}
	6	1.07×10^{-4}
	18	6×10^{-7} , 6.5×10^{-6} , 9.7×10^{-7}
	30	1.4×10^{-5} , 2.7×10^{-6} , 1.3×10^{-5}
$\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$	Zero	0.309, 0.139, 9.7×10^{-3}
	6	0.085, 0.022
	12	0.05, 6.5×10^{-3} , 0.024
	18	0.05, 0.019, 5.85×10^{-3} , 0.042
	24	0.045, 0.015
	30	0.04, 0.012
$\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$	Zero	0.05, 0.015
	6	5.06×10^{-5} , 1.47×10^{-5}

It is obvious from the above table that, the activation energies belonging to the nominal composition $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ possessed infinity small values with respect to those of normal semiconductors. On the other hand, the values of the activation energy are reduced much with transition from the higher to the lower range of dependence of resistivity on temperature.

4. Conclusions

1) Isothermal and hot pressing methods were used to prepare the system $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{O}_y$.

2) From $x = 0.0$ up to 0.5 , the isothermal hot pressed samples showed both semi metallic and semiconductor behaviors, whether the samples were as-prepared or post annealed.

3) Both high T_c 2223 and low T_c 2212 phases could be existed in the nominal compositions $0.0 \leq x \leq 0.5$.

4) Sintered samples of the nominal composition $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ post annealed at 820°C for 24 hours showed zero resistivity at $T_c = 134$ K. Other samples of the sintered one did not show any transition to zero resistivity.

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