

Doping of High-Temperature Superconductors

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Received 11.06.1998

Abstract

High-temperature superconducting ceramics systems YBaCuO and BiSrCaCuO, both doped by Pb, Sb, Li, K, Na and non-doped, have been produced by the method of solid phase reaction synthesis. The principle of controlled valency by Verwey has been used to characterize high-temperature superconductors. High-temperature superconducting ceramics have been obtained with properties stable in time by single-purpose doping.

Introduction

The discovery of superconductivity in the system La-Sr-Cu-O with the critical transition temperature into the superconducting state $T_c = 36$ K [1] stimulated an active search for high-temperature superconductors (HTSC) in a class of metal oxide combinations with rare-earths elements (REE). The superconducting transition was quickly [2] observed at 90 K in the system Y-Ba-Cu-O, while superconductors have been also obtained with other REE. Then the superconductivity at $T_c = 20$ K have been received in the system Bi-Sr-Cu-O [3]. The addition of calcium to this ternary structure led to discovery of superconductivity at 85 K [4] and evidence of superconductivity at 110 K [5] in the Bi-Sr-Ca-Cu-O system. Further investigations in this field resulted in discovery of superconductivity at 125 K in the system Tl-Ba-Ca-Cu-O [6].

The study of these materials is required both for the basic investigations to reveal the nature of high-temperature superconductivity [7] and to create electronic devices and systems on their basis [8].

This paper deals with the alterations of electronic states of atoms and their interdependence with the appearance of high-temperature superconductivity in systems Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O, using the results of tests and the principle of “controlled valency”.

Experimental Procedure

Non-doped and doped ceramic samples were prepared via the common method of solid phase reaction. Powders of Y_2O_3 , Bi_2O_3 , SrO_3 , $CaCuO_3$, $BaCO_3$, $LiCO_3$, Na_2CO_3 , K_2CO_3 , Sb_2O_3 and CuO were mixed in stoichiometric ratio to create nominal compositions (Table 1).

Table 1. Nominal composition of systems Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O

N	Chemical formula	Abbreviation	Temperature and time of annealing	Temperature and time of sinterizing
1.	$YBa_2Cu_3O_y$	123	900-940°C 70 hours	950 °C 36 hours
2.	$YBa_2Cu_{3-x}Li_xO_y$ x=0; 0.1 ; 0.3	123(Li) 123(Li)	"-" "-"	"-" "-"
3.	$YBa_{2-x}K_xCu_3O_y$ x=0.4	123(K)	"-"	"-"
4.	$Bi_2Sr_2Ca_2Cu_3O_y$	2223	800-810 °C 24 hours	840-850 °C 150 hours
5.	$Bi_{1.7}Pb_{0.2}Sb_{0.1}Sr_2Ca_2Cu_3O_y$	2223 (Pb,Sb)	"-"	"-"
6.	$Bi_{1.7}Pb_{0.3}Sr_{2+x}Ca_{4-x}Cu_5O_y$	2245 (Pb)	"-"	"-"
7.	$Bi_{1.7}Pb_{0.3}Sr_{1.7}M_{0.3}Ca_2Cu_3O_y$ M=Li, Na, K	2223 (M)	"-"	"-"

After being mixed according to their desired nominal compositions of Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O, the samples were pounded in corundum crucibles then placed into a furnace and annealed in air at temperature 900-940°C for about 70 hours and at 800-810°C for about 24 hours, respectively. The samples were removed from the furnace, pounded again and pressed under pressure of 10000 kg/cm². Afterwards, the pressed samples of Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O were replaced into the furnace and sinterized in air at temperature 950°C for about 36 hours and 840-850°C for about 150 hours, respectively.

Samples of 12.1.1 mm³ size were cut from the resulting ceramics to estimate the electrical properties. Silver paste was used to create the ohmic contacts needed to connect to them. The electrical properties were measured by standard 4-probe compensative method in the temperature intervals of 77-300 K during the direct and reverse thermal cycles. Direct current from 0.5 mA to 15 mA was admitted through the sample.

The samples were submitted to x-ray diffraction in CuK_{α} -radiation to determine their crystalline structure.

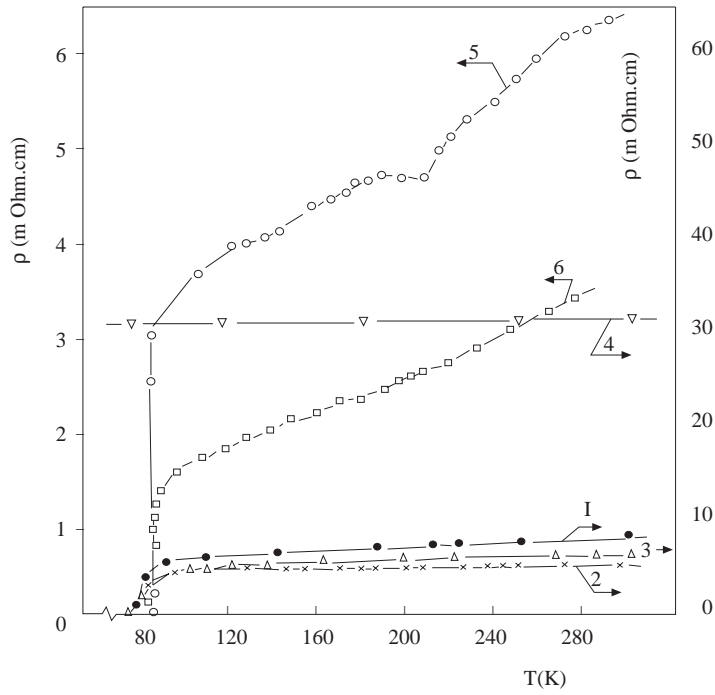


Figure 1. Temperature dependence of resistivity ρ of ceramics $YBa_2Cu_3O_y$.

1- non-doped,

2,3,4 - doped by lithium $YBa_2Cu_{3-x}Li_xO_y$,

x: 2 - 0.1; 3 - 0.3; 4 - 1.0

5,6 - doped by potassium $YBa_{2-z}K_zCu_3O_y$ $x=0.4$

5- measurements just after the synthesis,

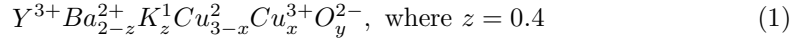
6- measurements after 2 years.

Results and Discussions

Figure 1 shows the changes of resistivity (ρ) as a function of temperature (T) for non-doped sample (curve 1) of phase 123 and samples doped by lithium (curves 2,3,4) and potassium (curves 5 and 6). The temperature of transition to superconducting state T_c and the transition width ΔT_c for lithium compositions $x=0, 0.1, 0.3$ are 85 K and 5 K, respectively. For the sample $YBa_2Cu_2LiO_y$ (curve 4) superconductivity was not observed in the investigated range of temperatures. While for samples doped by lithium

with $x=0.1$ and $x=0.3$ (curves 2 and 3) the resistivity has slightly decreased with regard to non-doped composition, the sample alloyed by lithium with $x=1.0$ (curve 4) has increased and no transition to superconducting state has been observed within the measured range of temperatures. Apparently it is due to the fact that, for small heterovalent replacement of 2-valent copper cation by 1-valent lithium ion, the concentration of Cu^{3+} holes in the CuO_2 layers increases, and with higher concentration the lithium ions replaces copper ions causing obstruction of current carriers to CuO_2 layers, that is, the 1-valent lithium cations obstruct the movement of electrons and T_c starts to decrease. It shows that, for HTSC YBaCuO of 123-phase, the maintenance of the translational symmetry of the CuO_2 layers is very important.

Curves 5 and 6 of Fig. 1 correspond to samples, doped by potassium. The doping has been accomplished by replacement of 2-valent barium ion by 1-valent potassium cation, i.e.



The resistivity close to the superconducting transition has decreased in comparison with the resistivity of non-doped state, but the temperature of transition to superconducting state has increased by 5 K, i.e. has become 90 K, and $\Delta T_c = 2$ K. The section on curve 5 in the temperature range 180-220 K is analogous to similar responses noted in the literature (see [9-11]).

When potassium ions are introduced into the sample using the mechanism of “controlled valency”, conditions are created where ions of different valencies appear in the same crystallographic positions. Copper ions have the most favourable thermodynamic conditions to increase their valency compared to the other ions of the given combination: Y^{3+} , Ba^{2+} , K^{1+} , Cu^{2+} . Hence, samples doped by the 1-valent potassium will have copper cations of different valency.

In Figure 2 variation in resistivity as a function of temperature in the phase 2223 for samples doped by Pb and Sb, measured at different times, are shown. The starting transition to superconducting state accounts for $T_{ce}=124$ K, and the final transition temperature is $T_{co}=106$ K, at which the resistance is zero. The critical temperature is $T_c=115$ K.

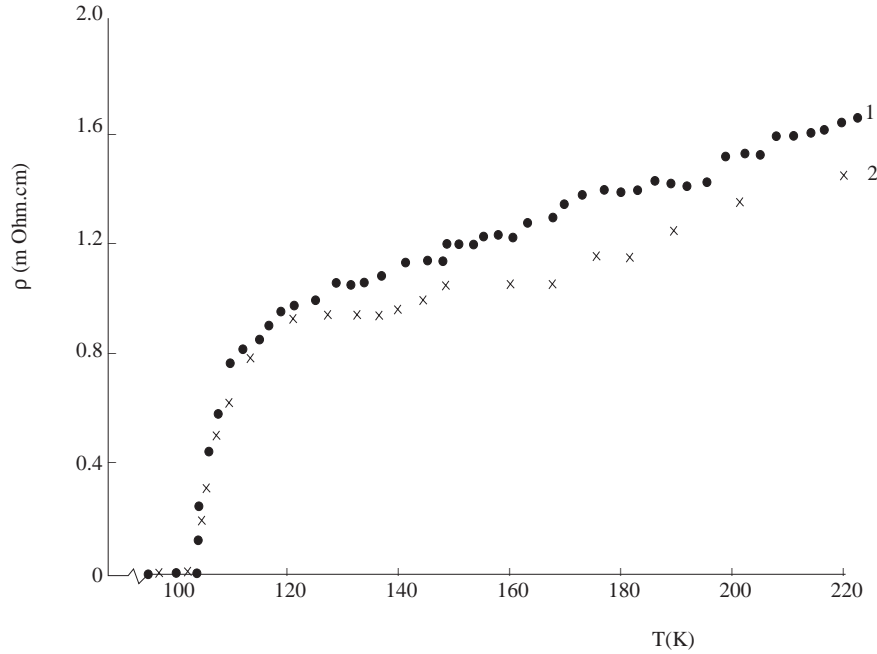


Figure 2. Temperature dependence of resistivity ρ for ceramics of $Bi_{1.7}Pb_{0.2}Sb_{0.1}Sr_2Ca_2Cu_3O_x$.

● - measurements just after the synthesis,

x - measurements after 2 years

At temperatures higher than T_c in the dependence $\rho(T)$, step changes in ρ is observed at 150, 170 and 200 K.

Reiterative measurements have shown that, for superconducting properties that were maintained over long periods of time, T_{co} remains unchanged at 106 K, with resistivity higher than T_{ce} decreased, which is due to the stabilization of the superconducting phase in time. However, as Figure 2 shows, the “steps”, remaintained after the reiterative measurements. The authors suppose that at temperatures 150, 170 and 200 K a copper valency change occurs and superconducting phases (in small amounts) have formed. Similar peculiarities of temperature versus resistance have also been observed in the other papers, but they were unstable. Our measurements show that the main phase at $T_{co}=106$ K, and the supplementary phases exposed by the above mentioned “steps”, are stable.

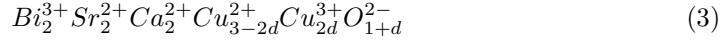
One should note that the partial replacement of bismuth by lead and antimony atoms permits synthesys of stable superconducting properties and an increase in T_c . With the partial change of copper valency from 2^+ to 3^+ , T_c develops a more direct dependence on the amount of Cu^{3+} ions [12]. In [13] the average value of copper valency, 2.35 for combination $Bi_2(Sr, Ca)Cu_2O_x$, has been estimated by x-ray photoemission. Such data are confirmed by tests of other authors [14]. They connect the appearance of superconduc-

tivity with the growing valency of the copper ions up to 3^+ , which constitute 20% of the copper atoms. However, in all of the above-mentioned papers the formation mechanism of the 3^+ copper ions remains unrevealed.

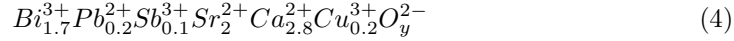
The appearance of the copper ions of different valency can be explained via the principle of “controlled valency”. The chemical formula of the bismuth ceramics is as follows:



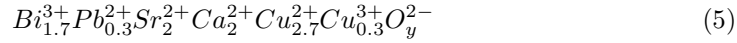
Hence, it shows the excess of oxygen of superstoichiometric composition, which causes the violation of electroneutrality of the crystal lattice. The components should increase their valencies in order to reconstruct electroneutrality in cation sublattices. From the thermodynamics point of view the Cu ions can increase their valency up to 3^+ . It can be approximately determined grounding on the potentials of ionization of elements. The copper ions have the least energy for 3-valency ion formation compared to the rest components. Therefore formula (2) can be presented as follows:



These processes, i.e. the increase of copper valency, lead to hole conductivity. However, in this system the excess oxygen is feebly connected. Under the influence of surrounding factors (heat, electrical, magnetic, optic, etc.) the amount of oxygen can be reduced to stoichiometric composition, and the amount of 3-valent copper ions will be reduced and superconductivity will be eliminated. Hence the purpose of doping is to learn the required amount of 3-valent copper ions. This can be accomplished by replacement of bismuth ions by 2-valent lead, taking into consideration the size ratios of replaceable ions. In this case, more favourable thermodynamic conditions to increase the copper valency up to 3^+ are created:



However, the combination doped by lead without antimony in non-stoichiometric composition is more stable and optimal:



This combination of mixed valency differs from combinations of non-stoichiometric composition by the filling of all lattice states, hence fewer defects are formed. The defect concentration of non-stoichiometric composition depends on the temperature due to the increase of entropy of lattice vacancies, as well as due to the partial pressure of ambient gas. However, in combinations of type (5) the dependence of concentration of charge carriers is slightly limited by temperature, ambient pressure and phase field. Therefore the investigated superconducting combination of bismuth system doped by 2-valent lead does not lose its superconductivity, for it is stable and does not depend on the ambient air pressure. It has been experimentally confirmed in many papers.

As for 3-valent antimony, it has no influence on superconducting properties of the combination, but only replaces the bismuth ion of the same valency. The electroneutrality of the lattice is not disturbed and the valency of ions does not change. Our concept with regard to antimony has been confirmed in many papers, published later. For instance, in [15] the influence of antimony on the properties of phase 2223 has been tested and no visible influence on superconductivity of combination 2223 has been exposed.

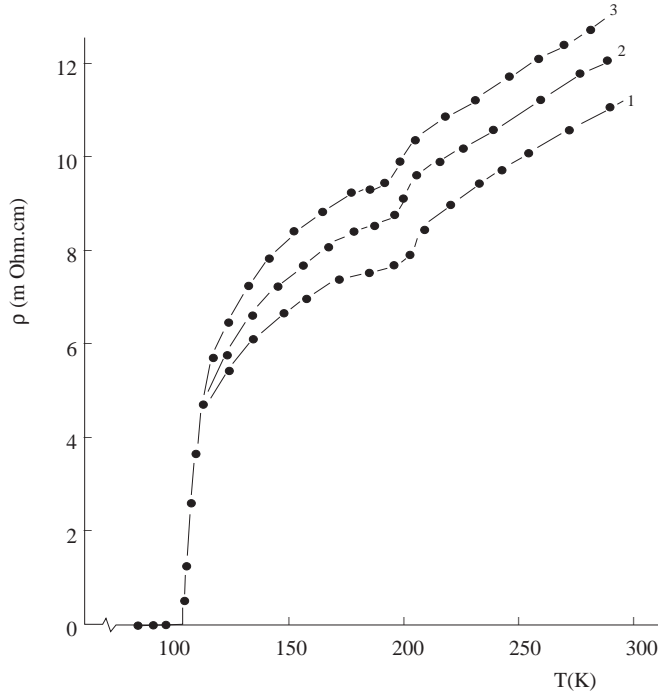


Figure 3. Temperature dependence of resistivity ρ of ceramics $Bi_{1.7}Pb_{0.3}Sr_{2+x}Ca_{4-x}Cu_5O_y$, $x:1 - 0.2; 2-0.6; 3-0.4$

In Figure 3 the change of resistivity depending on temperature for ceramics $Bi_{1.7}Pb_{0.3}Sr_{2+x}Ca_{4-x}Cu_5O_y$ doped by lead is shown. For all samples the transition to superconducting state begins at $T_{ce}=112$ K, and the final transition temperature is $T_{co}=102$ K. The critical temperature is $T_c=107$ K. It should be mentioned that the dependence $\rho(T)$ for all compositions ($x=0.2; 0.4; 0.6$) is practically the same.

For all samples in $\rho(T)$ dependence within the temperature range 120-200 K fracture is observed, resulting, we think, from the change of copper valency and formation of the other superconducting phase. Such fractures in $\rho(T)$ dependence have been registered by various authors [16], but only in samples of other composition. Reiterative measurements, carried out over 2 years, show that $\rho(T)$ dependence and the fracture for our samples do not change.

In Figure 4 the changes of resistivity from the temperature for ceramics $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_y$ doped by alkaline metals Li, Na, K are shown. Samples with Li and K additives start into the superconducting state at $T_{ce}=114$ K, and the final temperature, at which the resistance is zero, is $T_{co}=108$ K, with the critical temperature at $T_c=111$ K. In samples with Na additive $T_o=80$ K. All samples in the normal state possess metal-type conductivity.

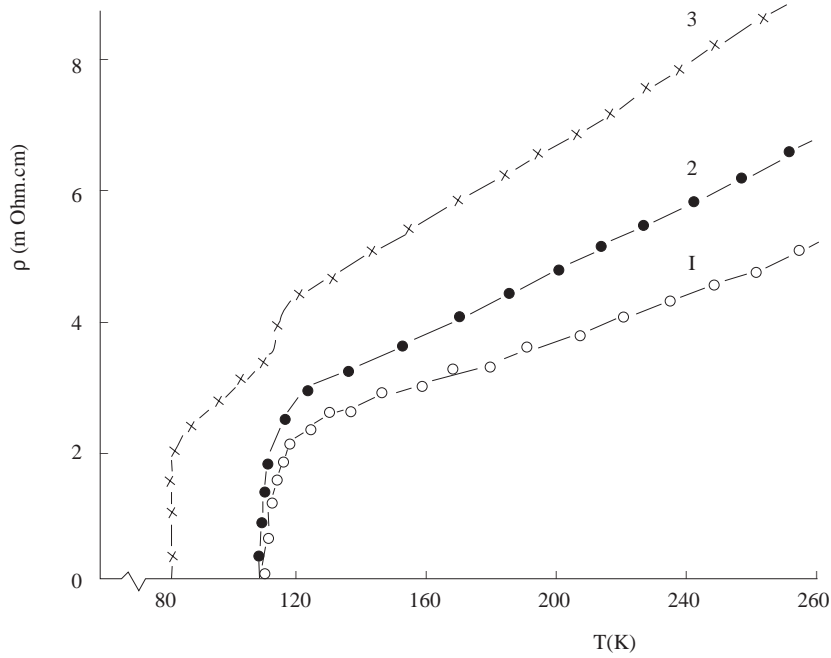


Figure 4. Temperature dependence of resistivity ρ of $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3A_{0.3}O_x$, A: 1-Li, 2-K, 3-Na.

Samples 2223 (Pb) without addition of alkaline metals had $T_{co}=106$ K. Addition of alkaline metals to $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_y$ leads to a complex change of the physical properties of superconductors. So Na decreases the temperature T_{ce} to 80 K and changes essentially the temperature dependence of electrical resistance in comparison with samples without additives. On curves of ρ -changes as a function of temperature the superconducting transition is observed to be caused by the 2212-phase. X-rays investigations have shown that in samples doped by Na different phases are formed, mainly the 2213 phase with $T_{ce}=80$ K.

Samples, containing Li and K maintain mainly the temperature dependence of resistivity typical of the sample without additives, but have less electrical resistivity in the normal state and higher T_{ce} value. On the curve of $\rho(T)$ dependence the single superconducting transition with the critical temperature 111 K is observed for these samples.

These results can show that the addition of the above mentioned elements in combination with lead stipulates the improvement of links on intergranular interfaces of high temperature 2223-phases. The decrease of transition width into the superconducting state ΔT_c gives witness to this fact.

Resistivity dependence on temperature under different magnetic fields for ceramics $Bi_{1.7}Pb_{0.3}Sr_{2.6}Ca_{3.4}Cu_5O_y$ are given in Figure 5. One can see that without the magnetic field the $\rho(T)$ dependence determines the sharp transition into the superconducting state within the temperature range 100-107 K. In addition, as Figure 5 demonstrates, the $\rho(T)$ dependence, over the various magnetic fields, shift to lower temperatures as the field grows.

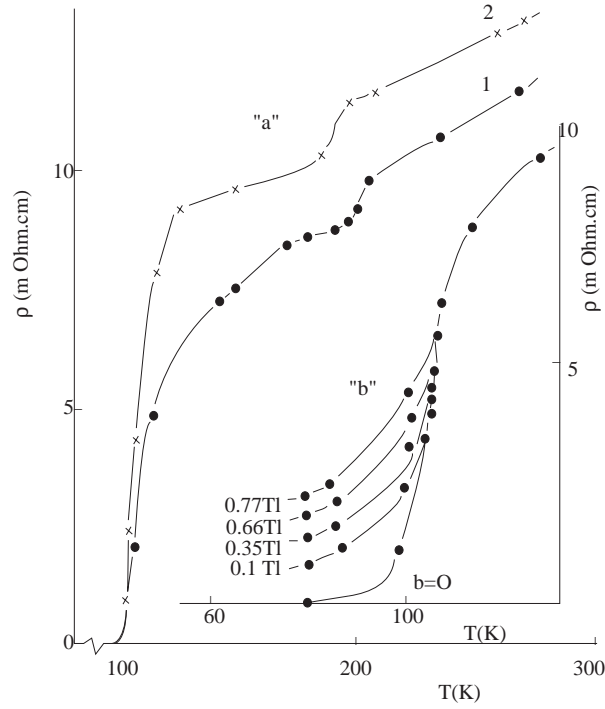
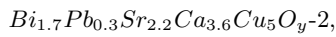
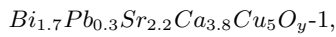


Figure 5. Temperature dependence of resistivity ρ of



a-without magnetic field, b-in various magnetic fields for ceramics $Bi_{1.7}Pb_{0.3}Sr_{2.4}Ca_{3.6}Cu_5O_y$

The T_c shift to the lower temperatures is also observed with the increase of current flowing through the sample.

For all other samples of bismuth composition, analogous resistivity dependence on temperature for similar magnetic field and current was observed.

Conclusion

In accordance with the observed data the doping of superconducting phases 123 and 2223 on the principle of “controlled valency” permits the synthesis of samples with superconducting properties stable in time and with increase in T_c . Thus as the valent state of copper changes from 2^+ to 3^+ , i.e. copper atoms change to a different valency with many being Cu^{3+} , higher the T_c . In turn, the increase in copper valency leads to the appearance of conductivity of p type. That is why the investigated ceramics with 123 and 2223 phases are hole materials.

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