DOPING HOLE CONCENTRATION AND T_C IN Ba- AND Pb-SUBSTITUTED $Bi-Sr-Ca-Cu-O$ COMPOUNDS
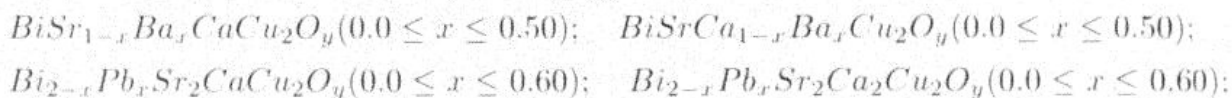
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The relation between T_C and doping concentration can be controlled by the substitution of ions Ba for Sr, Ca and ions Pb for Bi-contained superconductors. The liquid nitrogen quenching Pb doped samples showed T_C slight higher than that of furnace-cooled samples. The T_C reached maximum values at optimum holes concentration and there are changed by doping holes from one compound to another. The parabolic dependence of T_C on the doping concentration may be universal in many high-T_C superconductors cuprates.

1. Introduction

There is currently great interest in the relation between T_C and the density of holes in the CuO_2 planes in the p-type high-T_C cuprate superconductors. For samples of $La_{2-x}Sr_xCuO_4$ (214), the T_C has been presented as a function of total hole concentration as given by Sr content [1]. The total holes concentration may be replaced by the density of holes per CuO_2 plane, assuming that the holes are confined to the CuO_2 layers. In $YBa_2Cu_3O_y$ (123) the holes are distributed over the CuO chains [2]. The phase diagram for $YBa_2Cu_3O_y$ shows a broad dome-shaped curve with a maximum T_C of 90K. The question is a similar relation holds for the bismuth-containing cuprate superconductors? To this end we investigated the T_C of BSCCO-type compounds as a function of holes concentration.

It is found that the substitution of Ca and Sr by a (3+) ions cause a decrease of the hole concentration in CuO_2 plane in the $Bi_2Sr_2CaCu_2O_{y+\delta}$ [3]. The behavior of T_C versus doping holes on CuO_2 plane for several materials were also investigated. Usually this showed decrease in T_C at high doping concentration [4]. The distance between the two CuO_2 layers is correlated to the values of T_C has been reported in ref. [5]. This paper presents some results of studies on the following superconducting compounds.

$$BiSr_{1-x}Ba_xCaCu_2O_y(0.0 \leq x \leq 0.50); \quad BiSrCa_{1-x}Ba_xCu_2O_y(0.0 \leq x \leq 0.50);$$

$$Bi_{2-x}Pb_xSr_2CaCu_2O_y(0.0 \leq x \leq 0.60); \quad Bi_{2-x}Pb_xSr_2Ca_2Cu_2O_y(0.0 \leq x \leq 0.60);$$

The variation of T_C with doping hole concentration in these systems was performed. There is a comparison between our results with those of the others in some high-T_C superconducting cuprates.

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2. Experimental

The samples were prepared by solid state reaction method from starting powder-oxides of Bi_2O_3, $SrCO_3$, $CaCO_3$, $BaCO_3$, PbO and CuO. The mixed powder was dried at 100^0C for 1 hour in air, then grounded and cold pressed into the pellets. These pellets were sintered at 840^0C for 48 hours and annealed at 520^0C for the same time in air and then cooled in a furnace. The same the other samples were prepared by quenching from 840^0C into liquid nitrogen.

3. Results and discussion

Some our results of resistivity measurements on $Bi - Sr - Ca - Cu - O$ samples of $Sr-$ and $Ca-$ substituted by Ba element have been reported in ref. [6]. These experimental data showed that the superconductors were appeared in all composition of $x \leq 0.35$ for $BiSr_{1-x}Ba_xCaCu_2O_y$ and $BiSrCa_{1-x}Ba_xCu_2O_y$ compounds. The metallic property of $BiSr_{1-x}Ba_xCaCu_2O_y$ compound decreased by decreased x, but it was happende only in the temperature range about $120K$ for $BiSrCa_{1-x}Ba_xCu_2O_y$ compounds. It is possible that the change of metallic ratio of $Sr : Ca$ was originated for change of metallic property in those compounds.

The results of resistivity measurements for $BiSr_{1-x}Ba_xCaCu_2O_y$ and $BiSrCa_{1-x}Ba_xCu_2O_y$ compounds with $0.0 \leq x \leq 0.50$ showed that the superconductivity was appeared in all compositions of $0.0 \leq x \leq 0.35$. The metallic property of $BiSr_{1-x}Ba_xCaCu_2O_y$ compounds decreased by increasing x in the temperature range above $120K$ also it is found that in the compounds with $0.0 \leq x \leq 0.35$ at least two superconducting phases exist. There are superconducting transition temperatures of 85-90K for the lower phases and of $115-120K$ for the higher T_c phases. The maximum value of T_c for the higher T_c phases is observed around $x = 0.20 - 0.25$ and $0.20 - 0.30$ for $BiSr_{1-x}Ba_xCaCu_2O_y$ and $BiSrCa_{1-x}Ba_xCaCu_2O_y$, respectively.

The T_c value of the lower phase is nearly unchanged. By increasing x the resistivity curves of the $BiSr_{0.60}Ba_{0.40}CaCu_2O_y$ and $BiSr_{0.65}Ba_{0.35}CaCu_2O_y$ compounds were strongly changed. At compounds of $x > 0.40$ the resistivity curves exhibites semiconductor-like behaviour. The ac.susceptibility measurement of $BiSr_{1-x}Ba_xCaCu_2O_y$ and $BiSrCa_{1-x}Ba_xCu_2O_y$ compounds also indicated that the obtained transition temperatures were similarly in resistivity measurements. The superconducting signal is smedged at $x = 0.35$ and is completely vanished at $x > 0.40$. The diamagnetic fraction is largest at around $x = 0.25$ and decreases by increasing x.

It can be suggested that the hole concentration in CuO_2 plane reached the optimum value at around $x = 0.20 - 0.30$. The results of X-ray diffraction have indicated that the superconducting peaks of the samples with $x \leq 0.30$ could be identified with tetragonal structure. Their lattice parameters were very close to those of 2212- phase. It is found that the a- and c- axis slightly increased by increasing x. This is possibility that the difference in ionic radius between Ca, Sr and $Ba (Ca^{2+} < Sr^{2+} < Ba^{2+})$ is the reason of this effect. This is given conclusion that the substitution of Ba^{2+} ions larger than Sr^{2+}

and Ca^{2+} ions may contribute to an expansion of the lattice parameters in unit. However the investigated samples with limited doping concentration the tetragonal structure has not yet modulation in these compounds.

Dependence of Pb-substitution for Bi in $Bi - Sr - Ca - Cu - O$ (2212) and (2223) compounds has been studied. The variation of T_c with doping hole concentration of Pb^{2+} for Bi^{3+} was presented in table.1. These obtained results showed that for the cooled by furnace and quenched into liquid nitrogen samples of $Bi_{2-x}Pb_xSr_2CaCu_2O_y$ and $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_y$ with $x = 0.00 - 0.60$, we obtained the maximum values of T_c in the compounds at $x = 0.20 - 0.80$ by resistivity and ac.susceptibility measurement. XRD patterns showed that in the superconducting 2212- and 2223- phases have tetragonal structures. The lattices constants of these samples were obtained from X-ray diffraction. It is observed the lattice constants of the liquid nitrogen quenched samples were slightly large than those of the cooled samples by furnace in air for the both mentioned systems. According to ref. [7]. the hole concentration can be altered by action substitution. For example. When Y^{3+} substituted for Ca^{2+} and La^{3+} for Sr^{2+}, the hole concentration should be reduced. while substituting Pb^{2+} for Bi^{3+} it should be increased. In the both cases. our results were indicated that T_c should reached maximum value by increasing x and then decrease upon further doping. This character is accompanying by the change of valency of Cu in the compounds. According to the authors of ref. [8] the variation of T_c with x can not by simply explained by the dull change in the formal Cu-valency. rather it appeared to be correlated with the variation of the formal Bi- valency. too.

Table 1. The dependence of transition temperature on the doping hole concentrations with T_{c1} for (2223) and T_{c2} for (2212) superconducting phases.

| Samples	Composition	Cooled by funace		Quenched in liquid nitrogen	
	(x)	T_{c1}(K)	T_{c2}(K)	T_{c1}(K)	T_{c2}(K)
$Bi_{2-x}Pb_xSr_2CaCu_2O_y$	0.00	103	83	112	85.5
(2212)	0.10	109	84	115	84
	0.20	112	85	116	86
	0.30	117	86	120	86
	0.40	115	84	117	87.5
	0.50	107	82	113	85
	0.60	105	83	108	86.5
$Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_y$	0.00	112	82	115	87
(2223)	0.10	113.5	85	116	85
	0.20	115.5	84.5	118	86.5
	0.30	114.5	86	117	90
	0.40	113.5	84	116	86
	0.50	112	83	114	86
	0.60	110	82.5	112	85

The parabolic behaviors of T_c with doping hole concentrations have been demonstrated in figure.1a comparing with results in ref. [5] in figure 1b. In the $Bi-$ contained superconductors. the holes are confined to the O_{2p} orbital in the CuO_2 plane. Therefore

ie variation of holes by substitution in Bi- contained superconducting will be leading iriation of T_c as a function of holes concentration in CuO_2 plane. With increasing holes incentration T_c reached to maximum value and starts to decrease at the higher doping vels. Apart from this, the varying of hole concentration usually accompanied by new ansition [9, 10].
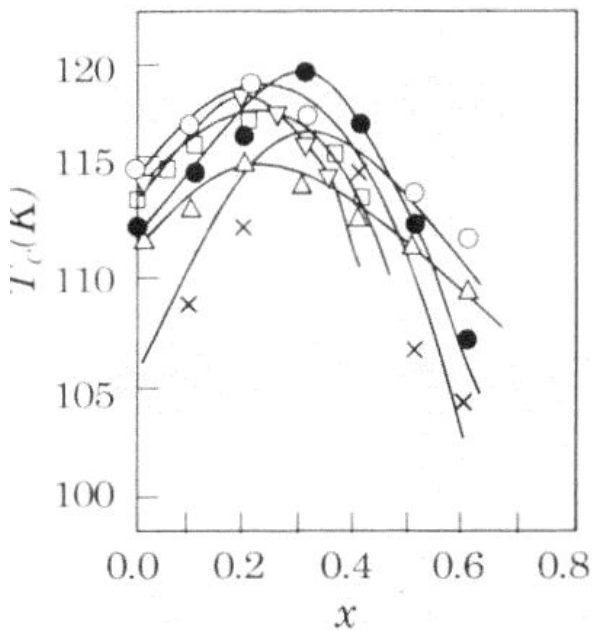
Fig. 1a Dependence of TC on the doping concentration (x).

$BiSr_{1-x}Ba_xCaCu_2O_y$ ( ):
$BiSr_{1-x}Ba_xCaCu_2O_y$ (V).
$Bi_{2-x}Pb_xSr_2CaCu_2O_y$ Cooled by furnace (×)
$Bi_{2-x}Pb_xSr_2CaCu_2O_y$ Quenched in nitrogen (●)
$Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_y$ Cooled by furnace (△)
$Bi_{2-x}Pb_xSr_2CaCu_2O_y$ Quenched in nitrogen (o)
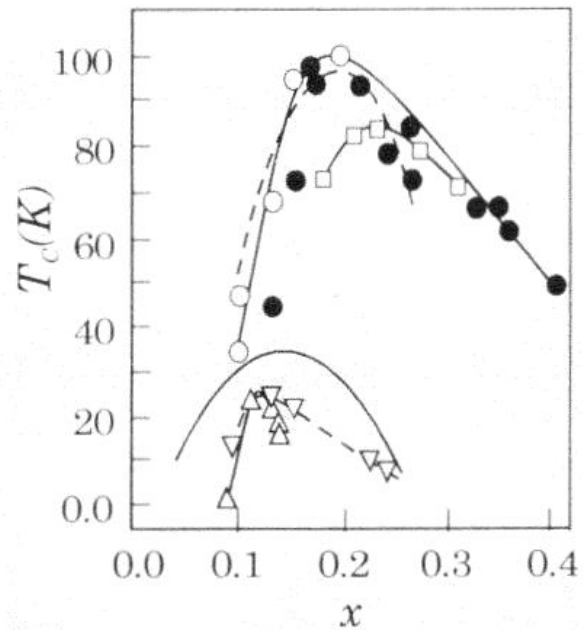
Fig. 1b Plot of T_c of superconducting cuprates containing one and two CuO_2 layers against the doping hole concentrations.

$La_{2-x}Sr_xCuO_y$ (×), $BiPbSr_{1-x}La_{1-x}CuO_y$ (△).
$Bi_2Sr_{2-x}La_xCuO_y$(V);
$Bi_2Ca_{1-x}(Nd,Y)_xSr_2Cu_2O_y$ (⊗);
$Y_{1-x}Ca_xBa_2Cu_2O_y$ and $Y_{2-x}La_xCu_3O_y$ (●);
$BiPbSr_2Y_{1-x}Ca_xCu_2O_y$ ( )

ummary: In the both investigated systems of $BiSr_{1-x}Ba_xCaCu_2O_y$ and $iSrCa_{1-x}Ba_xCu_2O_y$ we found that the superconductor-semiconductor transition at ≤ 0.10 and the Ba^{2+} ions caused the expansion in lattice parameters. For the systems of $Bi_{2-x}Pb_xSr_2CaCu_2O_y$ and $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_y$, the T_c values and lattice rameters of the quenched in liquid nitrogen slightly higher than that of cooled samples furnace. The superconducting transition temperatures (T_c) starts to decrease with reasing doping concentration (x) after reaching maximum value at optimum hole concentration and T_c dependence on hole concentration as a function of parabolic behavior.

In conclusion, the T_c has parabolic dependence on the doped hole concentration ay be universal in the superconducting cuprates with maximum values of T_c varying om one compound to the another (figure.1) But the presence of holes is not equate for perconductivity. It is explained for this there is not only interested in the change of Cu lency, but also the variation of the Bi- valency. In other word, the electron correlation tween the O_{2p} holes and Cu3d electrons must be taken into account.

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NỒNG ĐỘ LỖ TRỐNG VÀ NHIỆT ĐỘ CHUYỂN PHA SIÊU DẪN T_C TRONG CÁC HỢP CHẤT $Bi - Sr - Ca - Cu - O$ THAY THẾ Pb VÀ Ba

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Bài báo nêu lên mối quan hệ giữa nhiệt độ chuyển pha siêu dẫn (NĐCPSD) T_C và nồng độ lỗ trống thông qua quá trình pha tạp các ion Ba cho Sr, Ca và Pb cho Bi trong một số hợp chất siêu dẫn nhiệt độ cao (SDNĐC) chứa Bismuth. Kết quả cho thấy các mẫu pha tạp Pb được tôi trong Nit lỏng có NĐCPSD (T_C) lớn hơn so với NĐCPSD của các mẫu được làm nguội theo lò. ở những nồng pha tạp cao, siêu dẫn có thể biến mất. Giá trị T_C đạt được cực đại khi nồng độ lỗ trống tối ưu trong từng hợp chất. Đã tìm được sự phụ thuộc của NĐCPSD T_C vào nồng độ pha tạp có dạng parabol. Có thể cho rằng đặc trưng này là quy luật chung cho hầu hết các chất SDNĐC.