Unusual $T_c$ variation with hole concentration in Bi$_2$Sr$_{2-\delta}$La$_x$CuO$_{6+\delta}$

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We have investigated the $T_c$ variation with the hole concentration $p$ in the La-doped Bi 2201 system, Bi$_2$Sr$_{2-\delta}$La$_x$CuO$_{6+\delta}$. It is found that the Bi 2201 system does not follow the systematics in $T_c$ and $p$ observed in other high-$T_c$ cuprate superconductors (HTSC’s). The $T_c$ vs $p$ characteristics are quite similar to what observed in Zn-doped HTSC’s. An exceptionally large residual resistivity component in the inplane resistivity indicates that strong potential scatterers of charge carriers reside in CuO$_2$ planes and are responsible for the unusual $T_c$ variation with $p$, as in the Zn-doped systems. However, contrary to the Zn-doped HTSC’s, the strong scatter in the Bi 2201 system is possibly a vacancy in the Cu site.

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Many high-$T_c$ cuprate superconductors (HTSC’s) display an approximately parabolic dependence of $T_c$ upon the hole concentration $p$ with the maximum $T_c$ at $p \approx 0.16$. \cite{(p is defined as the hole concentration per Cu atom in CuO$_2$ planes.) This behavior was observed first in La$_{2-x}$Sr$_x$CuO$_4$. \cite{Then other HTSC’s such as YBa$_2$Cu$_3$O$_{7-\delta}$, Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, and Tl$_2$CaCu$_2$O$_{7+\delta}$ were also found to show approximately the same relation between $T_c$ and $p$ which scales only with the maximum $T_c$, $T_c$ max. Though not studied for the full range of $p$, several other HTSC’s are also known to have $T_c$ max at $p \approx 0.14 \sim 0.15$. \cite{Therefore one might expect that there possibly exists a universal relation between $T_c$ and $p$ which all HTSC’s satisfy.}

Existence of a universal parabolic relation between $T_c$ and $p$ for all HTSC’s, despite the different combinations of constituent atoms, the presence of various charge-carrier reservoir layers, and a variety of inter-plane coupling strengths, cannot be common but is believed to be related to a noble nature of high-temperature superconductivity. It is therefore not strange that the recent observations in Zn-doped HTSC’s of departure from the universal relation have drawn particular interest. \cite{Much attention has focused on the function of Zn. Within a HTSC, Zn substitutes for Cu in the CuO$_2$ plane and behaves as a nonmagnetic impurity without altering the carrier concentration. In this report, we show that a similar non-universal $T_c$ vs $p$ relation holds also for the La-doped Bi 2201 system, Bi$_2$Sr$_{2-\delta}$La$_x$CuO$_{6+\delta}$, which contains strong disorders in CuO$_2$ planes differing from impurities.}

We have obtained the hole concentration $p$ of the samples from the thermopower ($S$) measurements. The room-temperature thermopower $S$(290 K) of HTSC’s was found to be a universal function of $p$ over the whole range of doping, \cite{which has since been used widely to determine the $p$ of HTSC’s. The superconducting-transition temperature $T_c$ was determined at half the normal-state resistivity. The conventional solid-state reaction of stoichiometric oxides and carbonates was adopted in preparing polycrystalline samples of Bi$_2$Sr$_{2-\delta}$La$_x$CuO$_{6+\delta}$. The x-ray diffraction (XRD) analysis shows all the samples to be single phase to the threshold of detection. The oxygen content in the sample of $x = 0.1$ could be varied by annealing the same sample in vacuum for 6 h at different temperatures (400°C, 500°C, and then 600°C). $S$ was measured by employing the dc method described in Ref. 10. The resistivity $\rho$ was measured through the conventional low-frequency ac four-probe method.}

Figure 1 shows the temperature dependences of $S$ and $\rho$ of Bi$_2$Sr$_{2-\delta}$La$_x$CuO$_{6+\delta}$ (BSLCO) with $0.1 \leq x \leq 0.8$. The temperature and doping dependences of $S$ in Fig. \cite{(a) are typical of HTSC’s. $S$(290 K) increases with doping $x$ from $-15.5 \mu$V/K to 60 $\mu$V/K. Corresponding $p$ determined from the relations between $S$(290 K) and $p$ in Ref. 3 varies from 0.286 to 0.073 with doping. The $\rho$ measurements in Fig. \cite{(b) displays that the $T_c$ of BSLCO has its maximum at $x \sim 0.5$ or $p \sim 0.22$. The appearance of $T_c$ max at $x \sim 0.5$ agrees with the previous measurements. $T_c$ max is plotted in Figure 2. The $T_c$ (= 21.5 K) of $x = 0.5$ is used as $T_c$ max for solid circles. The dotted curve is of the universal relation, $T_c/T_c$ max, against $p$ is plotted in Figure 2. The $T_c$ ($= 21.5$ K) is also unusually low, which is only $\frac{1}{4}$ the $T_c$ of Tl$_2$Ba$_2$CuO$_{6+\delta}$, isostuctural of BSLCO. Taking the maximum $T_c$ of Tl$_2$Ba$_2$CuO$_{6+\delta}$ as $T_c$ max, BSLCO has much lower $T_c/T_c$ max’s, as represented by open circles in Figure 2. Unusual $T_c$ variation with $p$ is exposed more dramatically in the vacuum-annealed sample of $x = 0.1$ which superconducts at $T \leq 10$ K without vacuum-annealed. Vacuum annealing reduces the content of oxygen atoms interstitial between Bi-O planes and consequently $p$ in
CuO planes.\cite{9} Fig 3(a) shows that successive vacuum annealings at 400°C, 500°C, and then 600°C enhance $S$ of Bi$_2$Sr$_1.9$La$_0.1$CuO$_{6+\delta}$ from -15.5 $\mu$V/K to -9.3 $\mu$V/K. The corresponding variation of $p$ is from 0.286 to 0.240. We expect from the observed $T_c$-$p$ relation of BSLCO in Figure 2 that $T_c$ of the sample of $x = 0.1$ rises with annealing from 10 K to 20 K. The $\rho$ measurements in Figure 3(b), however, show that the superconductivity observed in the as-grown sample disappears with annealing in vacuum. We observed similar behaviors also in Bi$_2$Sr$_2$CuO$_{6+\delta}$ which had been prepared from the nominal composition of Bi: Sr: Cu = 2:2:1.5. The semiconducting as-grown sample of Bi$_2$Sr$_2$CuO$_{6+\delta}$ having $p = 0.282$ exhibited a superconducting-transition onset at 11.5 K when vacuum-annealed at 400°C. And yet subsequent vacuum annealings at 500°C and 600°C put the sample back in the semiconducting states. The $p$'s of the Bi$_2$Sr$_2$CuO$_{6+\delta}$ sample annealed at 400°C, 500°C, and 600°C were 0.256, 0.250 and 0.216 respectively, all of which are located in the superconducting region of Figure 3.

The $T_c$ vs $p$ characteristics of as-grown samples represented by the open circles in Figure 3 resemble those of Zn-doped HTSC’s in Ref. 6 and 7. It has been suggested that the primary effect of Zn impurities is to produce a large residual resistivity as a nonmagnetic potential scatterer in the unitary limit and that the more rapid depression of $T_c$ in the underdoped region is related to the large residual resistivity reaching the universal two-dimensional resistance $h/4e^2 \approx 6.5 k\Omega/\square$ per CuO$_2$ plane at the edge of the underdoped superconducting region.\cite{9} Unlike most HTSC’s, the Bi 2201 superconductor is found to have an exceptionally large residual resistivity.\cite{10,11} The corresponding two-dimensional residual resistance per CuO$_2$ plane ranges from 0.3 k$\Omega$/\square at an overdoped hole concentration to 10 k$\Omega$/\square at an underdoped concentration with 50% uncertainties.\cite{10,11} The large residual resistivity indicates that BSLCO contains strong scatterers of charge carriers in the planes. The strong scatterer in BSLCO is, however, not an impurity but most likely a vacancy in the CuO$_2$ plane, since any of Bi, Sr, and La can hardly substitute for Cu and disorders in the noncopper sites have little effect on superconducting properties but changing the hole concentration. Nevertheless, a vacancy in the CuO$_2$ plane is expected to act as a nonmagnetic potential scatterer, just like the Zn impurity in the planes. Vacuum annealing may cause extra vacancies in CuO$_2$ planes as well as expelling interstitial oxygen atoms. Thus the same argument in terms of disorder in the CuO$_2$ plane can be adopted for an explanation of the deeper suppression of $T_c$ in vacuum-annealed samples.

Although the above discussion does not provide a full account for the origin of the nonuniversal $T_c$ vs $p$ characteristics, it may be concluded that similarity between the Bi 2201 HTSC with disorders differing from impurities and other HTSC’s with Zn impurities seem to strengthen the argument that a strong potential scattering in the planes and a large residual resistivity at an underdoped hole concentration are closely related to the strong suppression of high-temperature superconductivity and the more rapid $T_c$ depression in the underdoped region.

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\[18\] Hole concentrations of the samples in Ref. 16 and 17 are estimated from the inplane resistivity at room temperature, $\rho_{ab}(300 K)$, and the temperature dependence of $\rho_{ab}$. A $\rho_{ab}(300 K) \approx 5$ m$\Omega$cm and a semiconductor-like temperature dependence at low temperatures of $\rho_{ab}$ usually appear in a sample with an underdoped hole concentration.
FIG. 1. (a) The thermopower $S$ and (b) the resistivity $\rho$ of Bi$_{2}$Sr$_{2-x}$La$_{x}$CuO$_{6+\delta}$ as functions of temperature. The numbers next to the curves denote the La content $x$ in the materials.

FIG. 2. $T_c$ of Bi$_{2}$Sr$_{2-x}$La$_{x}$CuO$_{6+\delta}$, normalized to $T_{c,\ max}$, plotted as a function of the hole concentration $p$ determined from the $S$ data in Figure 1 and the $S$-$p$ relations in Ref. 1. $T_{c,\ max} = 21.5$ K for closed circles and 85 K for open circles. The error bars show the upper limit of $T_c$ for the sample of $x = 0.8$ with $p = 0.098$. The dotted curve is a plot of the "universal" relation in Ref. 1.

FIG. 3. (a) $S$ and (b) $\rho$ of vacuum-annealed Bi$_{2}$Sr$_{1.9}$La$_{0.1}$CuO$_{6+\delta}$ as functions of temperature. The numbers next to the curves denote the annealing temperatures.