Doping \(n\)-type carriers by La-substitution for Ba in YBa\(_2\)Cu\(_3\)O\(_y\) system

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(Dated: March 23, 2022)

Thus far, there is no cuprate system where both \(n\)-type and \(p\)-type charge carriers can be doped without changing the crystallographic structure. For studying the electron-hole symmetry in an identical structure, we try to dope \(n\)-type carriers to YBa\(_2\)Cu\(_3\)O\(_y\) system by reducing oxygen content and substituting \(\text{La}^{3+}\) ions for \(\text{Ba}^{2+}\). Single crystals of La-doped YBa\(_2\)Cu\(_3\)O\(_y\) are grown by a flux method with \(\text{Y}_2\text{O}_3\) crucibles and it is confirmed that La actually substitutes \(\sim 13\%\) of Ba. The oxygen content \(y\) can be varied between 6.21 and 6.95 by annealing the crystals in an atmosphere with controlled oxygen partial pressure. The in-plane resistivity \(\rho_{ab}\) at room temperature was found to increase with decreasing oxygen content \(y\) down to 6.32, but interestingly further decrease in \(y\) results in a decrease in \(\rho_{ab}\). The most reduced samples with \(y = 6.21\) show \(\rho_{ab}\) of \(\sim 30\) m\(\Omega\) cm at room temperature, which is as much as seven orders of magnitude smaller than the maximum value at \(y = 6.32\). Furthermore, both the Hall coefficient and the Seebeck coefficient of the \(y = 6.21\) samples are found to be negative at room temperatures. The present results demonstrate that the non-doped Mott-insulating state has been crossed upon reducing \(y\) and \(n\)-type carriers are successfully doped in this material.

PACS numbers: 74.25.Fy, 74.72.Bk

High-\(T_c\) superconducting cuprates are classified into two types in terms of the sign of charge carriers: one has \(p\)-type charge carriers (hole-doped system) and the other has \(n\)-type ones (electron-doped system)\(^\text{1}\). The magnetic and superconducting phase diagrams of these types are known to be different from each other, and thus a whole phase diagram is conventionally drawn by connecting those at the non-doping point. However, discontinuity remains in the low-carrier limit, because there has been no prototypical system in which the type of carrier can be continuously changed from \(p\)-type to \(n\)-type while keeping an identical crystallographic structure. In the so-called “214”-type layered cuprates either electrons or holes can be doped; however, hole-doped 214 systems, for example, La\(_2\)−\(x\)Sr\(_x\)CuO\(_4\) (LSCO), have \(T^-\) or \(T^+\)-structure, whereas electron-doped 214 systems like Nd\(_2\)−\(x\)Ce\(_x\)CuO\(_4\) (NCCO) have different \(T^+\)-structure\(^\text{2}\). For the study of electron-hole symmetry in cuprates, it would be very useful if one could change the sign of charge carriers without changing the crystallographic structure unlike the case of 214 systems.

After the failure of various efforts to synthesize electron-doped cuprates, an empirical relation between the doping and crystallographic structures was proposed\(^\text{3}\). The coordination number of Cu atoms seems important for determining the sign of carriers; \(p\)-type carriers are favored with the coordination number of 5 or 6, while \(n\)-type ones are favored for 4-coordinated Cu. Indeed, it seems difficult to dope electrons to LSCO with \(T^-\)-structure\(^\text{4}\), or to dope holes to an infinite-layer system with 4-coordinated Cu atoms\(^\text{5}\). Furthermore, calculations of the Madelung potential\(^\text{6}\) are consistent with the behavior.

In YBa\(_2\)Cu\(_3\)O\(_y\) (YBCO), the oxygen content can be varied in a very wide range from hole-doped compositions to a non-doped insulating one. The doping can be varied also by chemical substitution\(^\text{7}\), for example, it is well known that substitutions of \(\text{Ca}^{2+}\) for \(\text{Y}^{3+}\) in the YBCO system increases the number of holes and shifts the doping range into overdoped regime\(^\text{8}\). On the other hand, \(\text{La}^{3+}\)-substitution for \(\text{Ba}^{2+}\) is expected to decrease holes. If the La-substitution for Ba is combined with the reduction of oxygen, the available doping range would shift across the non-doping point. This may allow one to study both the electron-doped and the hole-doped regimes in the same system, and the above empirical relation could be scrutinized.

In this work, we explore the ways to change the sign of charge carriers by combining the La substitution for Ba and the oxygen reduction in the YBCO system. In samples where La is substituted for 13% of Ba, we observe that the in-plane resistivity at room temperature becomes maximum at \(y = 6.32\), and further reduction to \(y = 6.21\) leads to a decrease in the resistivity down to \(\sim 30\) m\(\Omega\) cm, which is seven orders of magnitude smaller than the maximum value. Furthermore, these \(y = 6.21\) samples show both a negative Hall coefficient and a negative thermoelectric power, indicating that electrons are successfully doped.

Single crystals of La-doped YBCO are grown by a flux method using \(\text{Y}_2\text{O}_3\) crucibles\(^\text{9}\). In the starting material, \(\text{La}_2\text{O}_3\) is substituted for \(\text{BaO}_2\) by 10%, and \(\text{Y}_2\text{O}_3\) is provided by the crucibles. The purity of the raw material is 99.99% for \(\text{CuO}\) and 99.9% for \(\text{BaO}_2\), \(\text{La}_2\text{O}_3\) and \(\text{Y}_2\text{O}_3\) (crucibles). The actual composition of the grown crystals is analyzed by the inductively coupled plasma atomic-emission spectroscopy (ICP-AES) and is found to be \(\text{Y}_{0.38}\text{Ba}_{1.74}\text{La}_{0.88}\text{Cu}_3\text{O}_y\). Hence, La is substituted for both 13% of Ba and 62% of Y, so we express the composition as \(\text{Y}_{1-x}\text{La}_x(\text{Ba}_{1-x}\text{La}_x)_2\text{Cu}_3\text{O}_y\) with \(x = 0.13\) and
$z = 0.62$. Since Y and La ions have the identical valence number of +3, the carrier density should not depend on $z$. In this paper, we denote the specific composition of our single crystals of $\text{Y}_{0.34}\text{La}_{0.62}\text{(Ba}_{0.87}\text{La}_{0.13})_2\text{Cu}_3\text{O}_y$ by YLBLCO$_y$ for simplicity. The lattice parameters of as-grown crystals are determined to be $a=3.901$ Å and $c=11.763$ Å by the X-ray diffraction, where, interestingly, $a$ is much longer than pristine YBCO. In addition, no signal of any other phases is observed. The annealing is performed under various conditions shown in Table 1 by using a home-made furnace which can control the gas flow with a precise oxygen partial pressure. It should be noted that the oxygen control in our YLBLCO crystals is completely reversible between $y = 6.21$–6.95. Also, no structural transition, except for the ordinary orthorhombic-to-tetragonal transition, was suggested to be zero-resistance $T_c$ which was suggested to be $\sim 25$ K. The temperature dependence of the Hall coefficient [Fig. 1(b)] in YLBLCO$_{6.95}$ is found to be very close to that in YBCO$_{6.55}$, and this result suggests that the hole concentration of YLBLCO$_{6.95}$ corresponds to that of YBCO$_{6.55}$, which was suggested to be $\sim 7\%$ per Cu [Ref. 13]. Corroboratively, the slope of the temperature dependence of $\rho_{ab}$ in the YLBLCO$_{6.95}$ is similar to that in YBCO$_{6.55}$.

In YBCO system, there is no simple relation between the oxygen content and the exact hole concentration, because the latter depends also on the oxygen ordering in the Cu-O chain layers, as well as on how the positive charge is transferred from the Cu-O chains to the CuO$_2$ planes. Therefore, it is not simple to understand how the above two compositions produce an identical hole concentration. Nevertheless, the present result might be helpful for estimating the hole concentration of optimally-doped YBCO$_{6.95}$, because the effect of the oxygen ordering is quite modest in nearly fully-oxygenated samples. As mentioned above, the hole concentration of YLBLCO$_{6.95}$ is likely to be $\sim 7\%$/Cu, and thus in YBCO$_{6.95}$ it is inferred to be $\sim 20\%$/Cu by simple calculation (If so, the average valence of Cu in the Cu-O chain layers would be $+2.50$). We note that the actual hole concentration in the CuO$_2$ planes can be different from $\sim 20\%$/Cu, if the La-substitution affects the charge transfer from the chains to the planes.

The oxygen content of YLBLCO crystals can be decreased by reduction annealings. Figure 2 shows the evolution of the temperature dependence of the in-plane resistivity upon changing $y$ in a semi-log plot. $\rho_{ab}$ increases significantly with decreasing $y$ down to 6.32. In samples

![FIG. 1: The temperature dependences of (a) the in-plane resistivity and (b) the Hall coefficient in YLBLCO with $y = 6.95$, together with those for YBCO with $y = 6.55$.](image)

| $y$ | $T_{\text{anneal}}$ | duration | atmosphere | $T_c$ |
|-----|-------------------|----------|------------|------|
| 6.95 | 485               | 7 days   | 1 atm O$_2$ | 25   |
| 6.78 | 550               | 40 hours | 0.06 atm O$_2$ | -    |
| 6.43 | 550               | 40 hours | 2×10$^{-3}$ atm O$_2$ | -    |
| 6.32 | 700               | 12 hours | 2×10$^{-3}$ atm O$_2$ | -    |
| 6.29 | 750               | 12 hours | 2×10$^{-3}$ atm O$_2$ | -    |
| 6.21 | 890               | 6 hours  | 2×10$^{-3}$ atm O$_2$ | -    |

TABLE I: Annealing conditions for YLBLCO crystals. $y$ is the measured oxygen content.
with $y=6.32$, $\rho_{ab}$ at room temperature becomes as large as $\sim 10^6 \ \Omega \ cm$, which is about five orders of magnitude larger than that of La$_2$CuO$_4$ [Ref. 15]. We emphasize that the observed insulating behavior is not due to decompositions, because the samples can be re-annealed to another composition and give consistent results. When the oxygen content is decreased further from 6.32, interestingly, we observe a decrease in resistivity with decreasing $y$ [broken lines in Fig. 2].

Figures 3(a-c) show temperature dependences of the transport properties in the most reduced YLBLCO crystals with $y=6.21$. The in-plane resistivity in YLBLCO$_{6.21}$ becomes 30 m$\Omega$ cm at room temperature [Fig. 3(a)], which is seven orders of magnitude smaller than that in YLBLCO$_{6.32}$. The temperature dependence of $\rho_{ab}$ shows an insulating behavior below 300 K. The Hall coefficient shown in Fig. 3(b) is negative all the way below 300 K. The temperature dependence of $R_H$ is quite modest except at low temperatures, which gives confidence in estimating the carrier concentration from the 300-K value of $R_H$ to be $\sim 2\%$ per Cu [Ref. 16]. Furthermore, the Seebeck coefficient also shows a negative sign [Fig 3(c)]. These results clearly show that the sign of the charge carriers in this sample is negative. At the moment we cannot rule out the possibility that the n-type carriers are doped to the Cu-O chain layers rather than to the CuO$_2$ planes; however, such a possibility is very unlikely because the Hall mobility in YLBLCO$_{6.21}$, which is obtained to be 1.0 cm$^2$/Vs at 300 K, is comparable to that in YLBLCO$_{6.95}$ (2.7 cm$^2$/Vs) and pristine YBCO [Ref. 13]; such a high mobility of n-type carriers would not be expected in the Cu-O chain layers at $y=6.21$, at which the chains are very disordered and fragmented.

Figures 4(a) and (b) show the $y$ dependences of $\rho_{ab}$ and $S_{ab}$ at fixed temperatures. $\rho_{ab}$ shows a steep maximum at $y \sim 6.32$, where apparently there are few carriers. The Hall coefficient in this sample measured at room temperature is positive and $\sim 5 \times 10^4 \ \text{cm}^2/\text{C}$ within an error of $\sim 50\%$, which corresponds to the hole concentration of $\sim 1 \times 10^{-6}$ per Cu. These observations indicate that YLBLCO$_{6.32}$ is very close to the non-doped state. The sign of $S_{ab}$ correspondingly changes from positive to negative with decreasing $y$ across $\sim 6.3$ [Fig. 4(b)]. The absolute value of $S_{ab}$ appears to increase upon approaching the non-doped composition. Probably, $S_{ab}$ for $y=6.32$ is in the middle of a jump from positive to negative and happens to be intermediate. Similar behavior of the Seebeck coefficient is observed also in GdBaCo$_2$O$_{5+x}$ system, where continuous ambipolar doping is possible.

As discussed above, about 2% of electrons per Cu is successfully doped to YBCO system, but the system still remains insulating. Doping more electrons to this system is desirable, but unfortunately further reduction of YLBLCO has not been successful yet. One may guess that increasing $x$ is helpful for increasing n-type carriers. In this respect, we have also grown crystals with larger $x$ (= 0.18 and 0.32), but it turns out that low enough $y$ cannot be achieved in these high-$x$ samples. Hence, there is apparently a delicate balance between the $x$ value and
FIG. 4: Oxygen-content dependence of (a) the in-plane resistivity at 300 K and (b) the Seebeck coefficient at 280 K in YLBLCO. (c) Speculative phase diagram of YLBLCO.

the lowest achievable $y$ value. This is probably the main reason why this system has not been discovered as an electron-doped system. There still remains a possibility that optimizing the $x$ value allows further electron doping to make the system metallic and/or superconducting.

Figure 4(c) shows a speculative phase diagram for YLBLCO. In principle, one would be able to draw the phase diagram without discontinuity at the non-doping point just by determining the Néel temperature $T_N$ by a suitable means. We would like to emphasize that, to the best of our knowledge, this system is the first bilayer cuprate having $n$-type carriers.

Since the Cu atoms in the CuO$_2$ planes in the so-called “123” structure are 5-coordinated, it appears that the coordination number of Cu does not play a prohibitive role for determining the sign of charge carriers. Instead, the Cu-O bond length in the CuO$_2$ planes may be important, because that length in the present system ($\approx 1.95$ Å) is notably longer than that in other hole-doped cuprates and is almost equal to the NCCO system.

In conclusion, about 2% of $n$-type carriers are successfully doped in a Y-based bilayer cuprate in which La is substituted for Ba by 13%. In this system one can change the doping from $p$-type to $n$-type by reducing the oxygen content. Thus, we have, for the first time, spanned a doping range from negative to positive across the non-doping state in the same crystal. This opens a new avenue for studying the electron-hole symmetry (asymmetry) in cuprates.

This research was supported by the Grant-in-Aid for Science provided by the Japanese Society for the Promotion of Science.

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