Carrier-Controlled Doping Efficiency in $La_2CuO_{4+\delta}$

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We have studied the excess oxygen content and hole concentration in 110 °C annealed $La_2CuO_{4+\delta}$ prepared by electrochemical oxidation for $0 < \delta < 0.12$. Two distinct sites were observed with doping efficiency of 2 or 1.3 holes per excess oxygen atom. The occupation of the two different sites is determined by a critical carrier concentration $P_c \approx 0.06$. As a consequence, a sudden increase of chemical potential of doped holes at P_c is suggested. [S0031-9007(96)02000-5]

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La_2CuO_4, and antiferromagnetic insulator with a simple K_2NiF_4 layered crystal structure, becomes a prototype high-T_c superconductor upon cation substitution and/or anion doping. Although high temperature superconductivity was originally observed in the cation substituted $La_{2-x}Ba_xCuO_4$, the anion doped $La_2CuO_{4+\delta}$ exhibits far more interesting physical properties than its cation substituted counterpart. For example, onset T_c's as high as 45 K in bulk samples [1] and 60 K in thin films [2] were observed in electrochemically oxidized $La_2CuO_{4+\delta}$. Temperature-dependent distributions of the apical oxygen atoms, nonequivalent Cu-sites, microscopic segregation of holes, and macroscopic phase separation were observed and attributed to the intrinsic responses of $La_2CuO_{4+\delta}$ to doped holes [3–7]. In spite of extensive studies of this rich physical system, the fundamentally important issues such as the valence state of the interstitial oxygen atoms, the excess oxygen content (δ), and especially the corresponding hole concentration (p) have been controversial and are still largely unresolved. In this paper, we present our systematic studies of the excess oxygen content and corresponding hole concentration in 110 °C annealed $La_2CuO_{4+\delta}$ samples prepared by electrochemical oxidation for $0 < \delta < 0.12$.

The starting materials, La_2CuO_4 and $La_{1.95}Sr_{0.05}CuO_4$, were prepared by standard solid state reaction and subsequently oxidized by electrochemical oxidation methods previously reported [8]. To achieve a quantitative correlation between δ and Q, here Q is the charge transferred per formula unit, all intercalation reactions were performed below the oxygen evolution potential. The constant current method was used to charge samples up to $\delta = 0.08$ at room temperature. For $\delta > 0.08$, the potential step method was used with the cell temperature maintained at 70 °C. Electrochemical intercalation performed at elevated temperature greatly accelerates bulk diffusion which reduces the overpotential and therefore inhibits oxygen evolution at high δ values. After a sample was charged to a desired value of Q, the pellet was soaked in distilled water for 12 h with intermediate water changing and then washed several times in acetone. Finally, the sample was dried in vacuum for 12 h at room temperature. A sample prepared up to this stage is referred to as an “initial sample.”

The corresponding value of δ for a sample charged to Q was determined by the following procedure. A disk, with diameter ~0.6 cm and thickness ~ 0.06 cm, of mass ~80 mg of an initial sample was wrapped in Au foil (~20 mg). The pellet was then heated to 110 °C in air for 1 h to check that the sample had been thoroughly dried in vacuum. No weight losses were observed within our resolution of $\Delta W = \pm 2\ \mu$g. Finally, the pellet + Au foil was annealed at 550 °C in flowing nitrogen gas for 6 h and then furnace quenched. The final weight of the pellet is determined and the corresponding value of δ calculated. The residual excess oxygen content after annealing at 550 °C, determined by electrochemical deintercalation, is less than 0.0005. The uncertainties in the absolute δ values determined by weight loss experiments were estimated to be $\Delta\delta \sim \pm 0.002$ for δ below 0.08 and $\Delta\delta \sim \pm 0.003$ above 0.08.

In Fig. 1, the values of δ determined by weight loss experiments are plotted versus the corresponding charge transfer count Q obtained from the electrochemical oxidation experiments. The data are represented by a straight line according to the equation $\delta = Q/2$ up to $\delta = 0.11$. This result indicates that a single uniform overall electrochemical oxidation is operational up to $\delta = 0.11$ and that no electrochemical side reactions were involved even when samples were oxidized at 70 °C (samples with $\delta > 0.08$). At $\delta = 0.11$, where $p = 0.16$ as determined by iodometric titration, a substantial reduction of the current efficiency ($\delta \sim 0.1Q$) is observed. This indicates that the maximum oxidation state of $La_2CuO_{4+\delta}$ by oxygen doping is limited by the optimal hole doping concentration $p \sim 0.16$. This is consistent with the previous reports that a maximum effective hole doping ~0.16 is always observed independent of the starting material (La_2CuO_4 or $La_{2-x}Sr_xCuO_4$), prolonged oxidation time, and techniques

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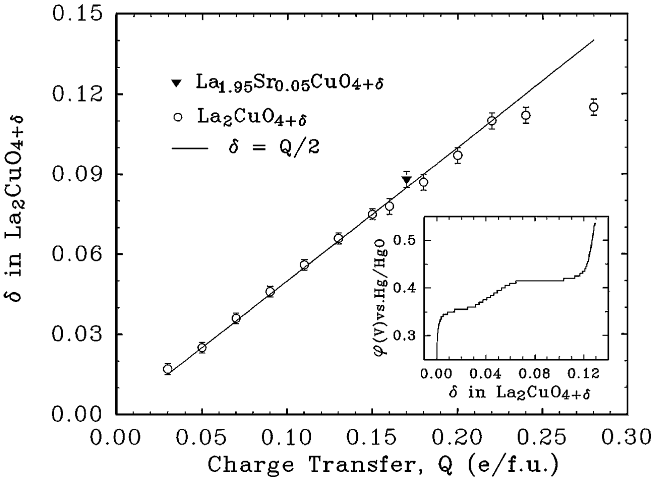

FIG. 1. Excess oxygen (δ) vs charge transfer (Q). The solid line represents the linear relation $\delta = Q/2$. δ and Q for a specific sample are independently determined by weight loss and electrochemical oxidation experiments, respectively. Inset: The potential step data for a sample charged to $\delta = 0.13$, where δ is determined by $\delta = Q/2$.

used for electrochemical oxidation [9,10]. The significant drop of current efficiency at $\delta > 0.11$ is related to oxygen evolution. In the inset of Fig. 1 we plot the potential vs δ for a sample charged to $Q/2 = 0.13$. It can be clearly seen that above $\delta = 0.11$ the potential increases rapidly to the oxygen evolution potential (~0.60 V vs Hg/HgO).

For the determination of p, the initial sample was first annealed at 110 °C under oxygen atmosphere for 24 h. To improve the accuracy and minimize error, the formal copper oxidation states in $La_2CuO_{4+\delta}$ and $La_{1.95}Sr_{0.05}CuO_{4+\delta}$ were determined by the ratio of the results of two titrations: First the copper concentration is determined and then the degree of oxidation above Cu^+ [11]. To prevent air oxidation of I^-, which introduces additional uncertainty in titration results, all the titrations were carried out in the presence of an ammonium acetate-acetic acid buffer [12]. Samples with each δ value were measured at least twice and in several cases six times. The average value determined for p, with an estimated uncertainty $\Delta p = \pm 0.005$, is plotted versus corresponding δ in Fig. 2. For $La_2CuO_{4+\delta}$ (open circle), the p vs δ behavior can clearly be divided into two linear regions with different doping efficiencies (holes created in the CuO_2 plane per intercalated oxygen atom). In the first region, for δ up to ~0.03, each excess oxygen atom contributes two holes to the CuO_2 planes. For $\delta > 0.03$ each additional intercalated oxygen atom contributes, on the average, 1.3 holes. The dotted line represents a doping efficiency of two holes per excess oxygen atom, and the solid line is the linear fit to the data points above $\delta = 0.03$. To elucidate the origin of this change of hole doping efficiency, we have prepared a series of cation and anion co-doped samples $La_{1.95}Sr_{0.05}CuO_{4+\delta}$. The δ's in $La_{1.95}Sr_{0.05}CuO_{4+\delta}$ were determined by the charge transfer Q according to $\delta = Q/2$. The δ value of one sample charged to $Q = 0.17$ was checked by a weight loss experiment (closed triangle in Fig. 1). Taking into account the initial Sr doping of 0.05, the behavior of p vs δ of co-doped samples is plotted in Fig. 2 (closed triangles) by shifting the horizontal axis by $\delta = 0.025$ (top horizontal axis). Each oxygen can be seen to contribute 1.3 holes when $p > 0.06$, and the data points fall on the solid line. This demonstrates that the critical hole concentration $p_c \sim 0.06$, not the excess oxygen content $\delta = 0.03$, determines the change of doping efficiency.

To further investigate the nature of the holes in $La_2CuO_{4+\delta}$, the hole concentration was also extracted from the room temperature thermopower data. It has been shown that there is an empirical universal correlation between the room-temperature thermoelectric power and the hole concentration for high temperature superconductors [13]. The thermoelectric power (S) of $La_2CuO_{4+\delta}$ was measured, and the corresponding hole concentration (p_s) was determined by comparing the results to similar room temperature data of $La_{2-x}Sr_xCuO_4$. The values of p_s are also plotted in Fig. 2 (closed circles). Both the value of p_s and the p_s vs δ behavior are identical to that determined by titration up to $\delta \sim 0.08$. The same critical $p_c \sim 0.06$ for the change in the doping efficiency is again observed in p_s vs δ. Therefore at room temperature the electronic system of holes induced by excess oxygen is similar to that induced by doping with strontium over a considerable range of doping levels. The observation that the transport properties, at a very limited low doping level, are quite

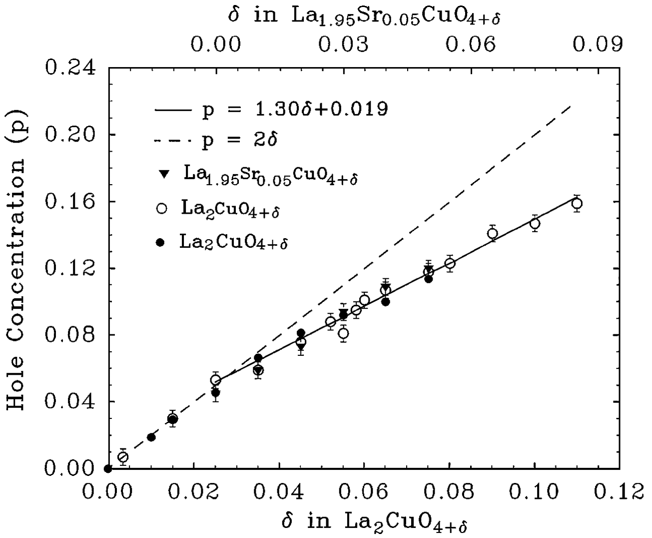

FIG. 2. Hole concentration (p) vs excess oxygen content (δ). (○) $La_2CuO_{4+\delta}$, from titration results; (●) $La_2CuO_{4+\delta}$, from thermopower measurements; and (∇) $La_{1.95}Sr_{0.05}CuO_{4+\delta}$, from titration results. Dotted line represents two holes per oxygen atom and solid line is the linear fit to the titration data (open circles) for $\delta > 0.03$.

similar for strontium-induced and oxygen-induced holes in La_2CuO_4 [14] agrees with our conclusion. The details of the method of extracting P_s and an analysis of the temperature dependence of S for the whole series of $La_2CuO_{4+\delta}$ samples will be published elsewhere [15].

The existence of the critical hole concentration $p_c \sim 0.06$ and the lack of any corresponding anomaly in Fig. 1 indicate that the change in doping efficiency is electronic in origin. It should be noted that the critical concentration p_c is at the hole concentration where the conductivity versus temperature behavior of all high T_c layered cuprates becomes metallic around room temperature and superconducting at low temperature [16,17]. Therefore the doping efficiency is controlled by the intrinsic characteristics of the electronic system of $La_2CuO_{4+\delta}$: Two holes are created in the CuO_2 plane for each excess oxygen atom ($O_{(2)}$) in the insulating region and 1.3 holes per additional excess oxygen atom ($O_{(1.3)}$) in the metallic region. In Fig. 2 the finite intercept of 0.019 in the doping efficiency equation $p = 1.3\delta + 0.019$ for $p > 0.06$ indicates that both $O_{(1.3)}$ and $O_{(2)}$ co-exist in the metallic samples. Consequently, there are two bonding configurations with the binding energy of $O_{(2)}$ being different from that of $O_{(1.3)}$. Indeed, two distinct peaks were observed in our gas effusion spectra of $La_2CuO_{4+\delta}$. The gas effusion experiment is performed by continuously heating a $La_2CuO_{4+\delta}$ sample at a rate of 20 °C/min in a sealed quartz tube under vacuum and recording the total gas pressure as a function of temperature (inset in Fig. 3). The δ values determined in the gas effusion experiments were consistent within 10% with the values determined by weight loss and the electrochemical charge transfer. In Fig. 3 we present the gas effusion spectra of $La_2CuO_{4+\delta}$ for $\delta = 0.015$, 0.055, and 0.075. Two oxygen peaks can be clearly seen at ~260 and ~420 °C. Although both peaks grow initially at low δ value, the oxygen content under the second peak (δ_2) saturates at $\delta_2 \sim 0.033$ (the shaded area in Fig. 3), while the oxygen content under the first peak (δ_1) continues to grow. This systematic behavior is observed for the whole composition range ($0 < \delta < 0.11$) we investigated. This result is consistent with the doping efficiency data since the initial ~0.03 $O_{(2)}$ excess oxygen atoms should remain the same at high δ values. For $\delta = 0.015$, the small peak observed at 260 °C is probably due to the thermal activation of the excess oxygen atoms under the second peak into the first peak. However, δ_2 becomes thermally stable after it is saturated. Two similar gas effusion peaks are also observed in $La_{2-x}Sr_xCuO_{4+\delta}$, where $x = 0.025$, with a stable saturation $\delta_2 \cong (P_c - x)/2$. This indicates that $O_{(2)}$ ions are coupled to the electronic system and become stabilized at Pc. In Fig. 4, we plot δ_2 vs δ of $La_{2-x}Sr_xCuO_{4+\delta}$ for $x = 0$ and 0.025. It can be clearly seen that for a fixed x, δ_2 increases with δ initially and saturates at $\delta \cong 0.033$ and 0.018, respectively. However, δ_1 continuously increases. The details of the gas effusion studies of $La_2CuO_{4+\delta}$ will be reported later [18].

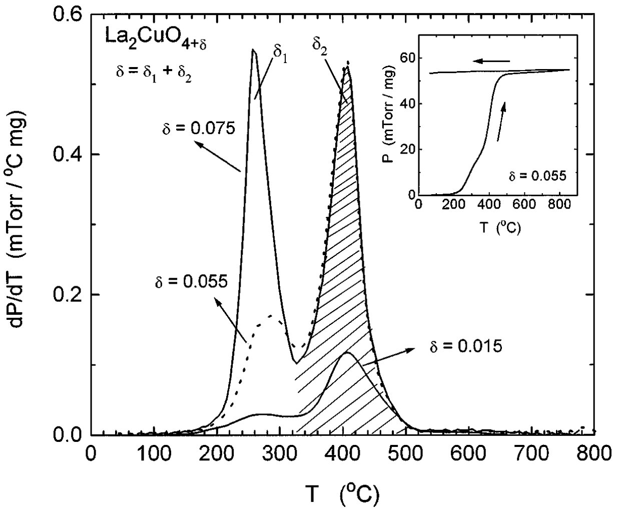

FIG. 3. Gas effusion spectra of $La_2CuO_{4+\delta}$ for $\delta = 0.015$, 0.055, and 0.075. Inset: The evolved gas pressure as a function of temperature for $\delta = 0.055$. Gas effusion spectra were obtained by taking temperature derivatives of the pressure vs temperature curve.

Although two holes per excess oxygen can easily be understood if we assume that the interstitial oxygen is an $O^{=}$ ion, 1.3 holes per excess oxygen is quite peculiar. We offer one possible explanation here: It has been suggested by the neutron diffraction studies of both La_2CuO_4 and La_2NiO_4 that interstitial oxygen can form either short O-O bonds with some peroxide character or, alternatively, a polyoxide $O_3{}^{5-}$ complex with one or two neighboring apical oxygen atoms, respectively [19,20]. Either of the above scenarios can effectively reduce the net doping to less than two holes per excess oxygen atom. For instance, each excess oxygen atom

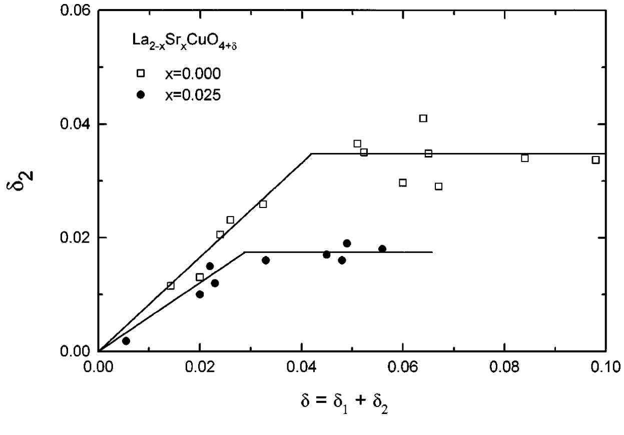

FIG. 4. The excess oxygen content under the second peak (δ_2) vs total excess oxygen content ($\delta = \delta_1 + \delta_2$), where (□) $x = 0.000$; (●): $x = 0.025$. δ_2 saturates at a value with $\delta_2 \cong (P_c - x)/2$.

will effectively contribute one hole to CuO_2 planes if it forms ${O_3}^{5-}$ complex with two apical oxygen atoms. Therefore the average doping efficiency of 1.3 can be understood as a global arrangement of bonding configuration (long range correlation) of those oxygen atoms such that two out of every three excess oxygen atoms will form polyoxide complex. In this case, on the average, there will be four holes doped for every three excess oxygen atoms. Since peroxy species are not detected for kinetic reasons in the reaction with I^-, an average doping efficiency of $\sim$1.3 results from titration experiments. Thermal annealing, although at only 110 °C, facilitates redistribution and equilibration of oxygen atoms to form peroxy species, leading to the observed p vs δ behavior. Further investigations are underway to verify the above suggestion.

It is noted that, although there exist qualitative and quantitative differences, two oxygen effusion peaks at the same positions as those in the gas effusion spectra in $La_2CuO_{4+\delta}$ are also observed in those of the isostructural $La_2NiO_{4+\delta}$ [18]. Therefore the two bonding configurations observed are characteristic to the structure. A natural consequence of this observation is the existence of a finite jump in the chemical potential of doped holes at p_c. It has been shown that in $YBa_2Cu_3O_{6+x}$, thermodynamic quantities corresponding to doped oxygen atoms, such as chemical potential μ, fractional site occupancy, and $kT(\partial x/\partial \mu)_T$, can by quantitatively accounted for only by explicitly taking into account the effects of doped holes [21]. Therefore the thermodynamic behavior of doped oxygen atoms is a reflection of the behavior of the chemical potential of the doped holes. As holes are created one by one on the insulating antiferromagnetic background of CuO_2 planes by doping, the chemical potential of doped holes varies very slowly as a function of p or remains at a constant value up to $p_c \sim 0.06$. A sudden jump of the chemical potential at p_c forced the subsequently doped oxygen atoms to adopt a different configuration with a characteristically different doping efficiency $\sim$1.3. Although the origin, the magnitude, and the behavior of this jump are not clear yet, the existence of this sudden increase of the chemical potential of holes at p_c imposes a severe restriction on the microscopic models for the occurrence of high T_c in layered cuprates. Our data, obtained at finite temperature, cannot distinguish if this jump in chemical potential is continuous or discontinuous.

In summary, we have studied the excess oxygen content (δ) and corresponding hole concentration (p) in 110 °C annealed $La_2CuO_{4+\delta}$ prepared by electrochemical oxidation for $0 < \delta < 0.12$. A quantitative correlation of $\delta = Q/2$ is observed up to $\delta = 0.11$. Within our experimental uncertainty of $\Delta p = \pm 0.005$, the doping efficiency can be described by two distinct linear regimes: (1) $p = 2\delta$ up to $\delta \sim 0.03$; and (2) $p = 1.3\delta + 0.019$ for $0.03 < \delta < 0.11$. The change in doping efficiency from 2 holes per excess oxygen atom to 1.3 holes per excess oxygen atom occurs at a critical hole concentration $p_c \sim 0.06$, which is characterized by a sudden increase of chemical potential of doped holes.

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