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ELECTROCHEMICAL OXIDATION OF La_2CuO_4 SINGLE CRYSTALS*

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Bulk superconducting $La_2CuO_{4+\delta}$ single crystals are obtained by using electrochemical intercalation technique from the as-grown insulating samples. Oxidation is carried out by constant current I=10μA at temperature $T = 70°$C and room temperature, respectively. Structure and magnetic properties are studied by low-temperature X-ray diffraction and susceptibility measurements. A superconducting phase with T_c of 19K and δ-0.12 can be attributed to the formation of oxygen clusters. Room temperature oxidation is inhomogeneous: two superconducting phases with T_{c1} of 24K and T_{c2} of 8K and an antiferromagnetic phase are coexisting in the crystal. It is found that the appearance of T_c in this system has the "step" tendency.

Keywords: electrochemical oxidation, La_2CuO_4 crystals
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I. INTRODUCTION

It is well known that La_2CuO_4 has been extensively used as a host material for oxygen insertion study because of the relative simplicity of its structure and chemical composition. Oxygen can be intercalated into La_2CuO_4 by many methods, such as high pressure-oxygen annealing[1], chemical oxidation[2], electrochemical oxidation[3] and annealing in ozone.[4] Among all the techniques, electrochemical intercalation presents a unique advantage of precise control of excess oxygen content δ to the highest value δ-0.12 with an onset superconducting transition temperature of 45K.[3]

The phase diagram of $La_2CuO_{4+\delta}$ system shows many interesting features. There are several miscibility gaps due to the mobility of intercalant oxygen ions.[5] When $0 \leq \delta \leq 0.055$, a macroscopic phase separation has been observed near room temperature and it produces a mixture of oxygen-poor antiferromagnetic La_2CuO_4 phase and oxygen-rich superconducting $La_2CuO_{4.08}$ phase.[5] Recently, single crystal neutron diffraction studies on compositions with δ <0.06 show staging behavior. Evidence for stages of 2,3,4,6.6,7 have been obtained so far.[6] An additional in-plane ordering of the interstitial oxygen upon slow cooling to below 215K has been observed in a $La_2CuO_{4.015}$ crystal.[7] The low-energy incommensurate spin fluctuations in $La_2CuO_{4+\delta}$ with stage-6 have also been studied.[5] When $\delta \geq$0.055, metastable phases with T_c >34K, such as T_c-45K (or 42K) phase will appear. On annealing between 25°C and 110°C, these phases decompose into two phases with T_c's of 30K and 15K without change in the oxygen content.[8]

$La_2CuO_{4+\delta}$ is a complex system both electronically and structurally. Further understanding of the electronic properties requires detailed studies of the structure using high quality crystals. Chou *et al.*[9] reported the preparation and characterization of electrochemically oxidized single crystals of $La_2CuO_{4+\delta}$ with T_c-32K and/or 40K for the first time. Due to the difficulties in preparation, there are fewer reports on crystals than those on the ceramic materials by electrochemical oxidation. In this paper, we report results on electrochemical intercalation of oxygen into La_2CuO_4 crystals.

II. EXPERIMENTAL

The undoped La_2CuO_4 crystals were grown using a CuO flux method as described in Ref.[10]. Two crystals, crystal A with mass 8.6mg ($\sim 2 \times 1 \times 0.7$ mm^3) and crystal B with mass 36.9mg ($\sim 4.5 \times 2 \times 1$ mm^3) were subjected to electrochemical oxidation.

The electrochemical cell was set up as La_2CuO_4/1M NaOH/Pt, where the positive working electrode was a single crystal of La_2CuO_4 and the negative counter electrode was a gold foil. The reference electrode was Hg/HgO/1M NaOH electrode (E_0=

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+0.098V vs. normal hydrogen electrode). The electrolyte should be constantly stirred to maintain constant electrolyte concentration around the working electrode. A platinum wire was attached to one side of the single crystal using gold paint. The gold paint was then left to dry at room temperature for 2h. The crystal with attached electrode was annealed at 500°C for 4h to remove the organics present in gold paint, and furnace cooled to room temperature.

An anodic current of 10μA was applied to the working electrode. Oxidation of crystal A was carried out at elevated temperature T=70°C for 1 month and crystal B was performed at room temperature for 2 months. The charging time required for a single crystal to reach a single phase is much longer than for polycrystalline samples. Evidently the smaller specific surface area and the long diffusion distance from crystal surface to the interior is responsible for the slower charging process in single crystals.[9]

At the end of the experiments, the crystals were washed in acetone and purified water to remove any residual electrolyte left on the surface of the crystal.

Magnetic susceptibility measurements were made by using a superconducting quantum interference device (SQUID, Quantum design MPMS, 5.5T) magnetometer with the field applied perpendicularly to the CuO_2 planes. Superconducting transitions were determined by Meissner effect (field cooling) and shielding signal (zero field cooling) when a low magnetic field of 0.0015T was employed. High magnetic field of H=0.05T to 0.5T was applied to detect the antiferromagnetic (AF) ordering. X-ray diffraction data were collected in the temperature range from room temperature to 9K using an MXP-AHF18 X-ray diffractometer with a low-temperature attachment.

Ⅲ. RESULTS

The shape of characteristic cyclic voltammogram obtained in our crystal is the same as the one for ceramic materials previously reported in Ref.[3]. The typical potentiodynamic I/E profile of a La_2CuO_4 single crystal in 1M NaOH electrolyte with sweep rate 5mVs^{-1} at room temperature is shown in Fig.1. In the anodic sweep, a broad peak in the region 150mV$\leq E \leq$ 500mV can be seen in the I-E curve. The increase of current is mainly due to oxidation of Cu(II) to Cu(III) in this region.[11] Afterward, the current starts to build up steeply because of copious O_2 evolution when E >600mV. The oxidation plateau in I-E curve of La_2CuO_4 single crystal is shown for the first time in our paper, which indicates that oxidation mechanism during oxygen intercalation process for the single crystal is the same as that of ceramic materials. The global reaction can be written as[9]:

$$La_2CuO_4 + 2\delta OH^- \rightarrow La_2CuO_{4+\delta} + \delta H_2O + 2\delta e^-.$$

The La_2CuO_4 compound has a layered structure of alternating planes of CuO_2 and La_2O_2,[12] which suggests that when the sample is oxidized, electrons are coming out from the CuO_2 planes and O^{2-} ion is intercalated to maintain electroneutrality.

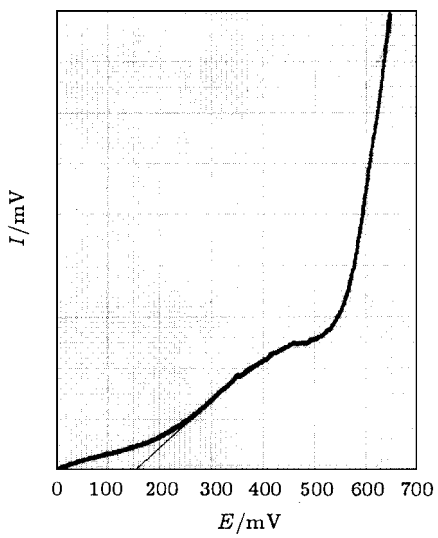


Fig.1. Potentiodynamic I/E profile of La_2CuO_4 single crystal in 1M NaOH electrolytic solution. T=298K, sweep rate ν=5mVs^{-1}.

It is suggested that the oxygen anions move from one layer to another while diffusing towards the bulk of the crystal. This hopping process is expected to have appreciable activation energy because there is a strong interaction between the diffusing species and the lattice.[13] Because the rate of electron transfer is faster than that of O^{2-} ion diffusion during the intercalation process, inhomogeneous concentration of O^{2-} ions from surface to inner part of the crystal has been observed.[14] However, oxidation at elevated temperatures can increase the oxygen ion mobility and obtain a sample close to equilibrium during the oxidation process.[15]

Figure 2 shows the temperature dependence of magnetization for crystal A which is oxidized at 70°C. A diamagnetic signal is shown in field cooling (FC) data and zero field cooling (ZFC) data. There is only one superconducting transition at T_c ~19K, which is much lower than usually reported value (~30K or

45K) in the $La_2CuO_{4+\delta}$ system. The value of ZFC magnetization at 5K for this crystal is large while the FC signal is low. This phenomenon has been observed in most high-T_c superconducting single crystals and may be due to flux pinning from precipitates, twin boundaries and/or cracks in the crystals. Crystal A is bulk oxidized, there is no antiferromagnetic (AF) peak observed at the Néel temperature around 250K as shown in the inset of Fig.2. The peak at T-50K originates from the frozen-oxygen in magnetometer sample chamber when temperature decreases.

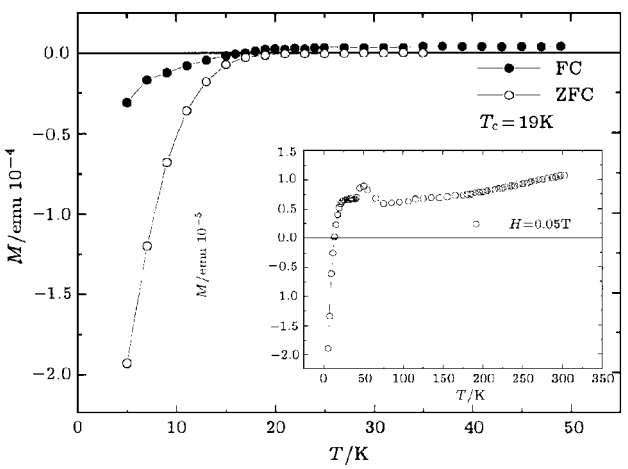


Fig.2. Temperature dependence of magnetization for crystal A in low field H=0.0015 T. Data are shown in ZFC and FC mode. The inset shows the magnetization as function of temperature in field H=0.05T.

A phase with low T_c of 12K has also been observed in a $La_2CuO_{4.03}$ single crystal, whose superconductivity is evidenced to have no connection with phase separation.[16] It is explained by the fact that the actual physical segregation in $La_2CuO_{4+\delta}$ system ($0 \leq \delta \leq 0.055$) is governed by kinetics (oxygen mobility) and may be delayed in high-quality crystals. It is quite possible that the oxygen mobility in the high-quality crystal is low enough to form detectable nuclei of the phase-separated new oxygen-rich phase in the region where the excess oxygen concentration is inside the miscibility gap.[16] It is known that sample quality is crucial for the oxygen diffusion process. In Ref.[17] it has been shown that oxygen insertion in $La_2CuO_{4+\delta}$ thin films first happens mainly along planar faults and dislocations, and only after this does a very slow oxygen diffusion along the interstitial sites take place. The oxygen mobility is diminished in high-quality single crystals because of the lack of structural channels for diffusion process. As a result, it is possible to get macroscopically nonseparated superconducting crystals whose excess oxygen concentration is inside the miscibility gap.[16]

However, the possibility of the above explanation for low T_c (~19K) in crystal A of our experiment is ruled out. Because the oxygen content δ of crystal A is beyond the miscibility gap. After oxidation, the c-axis of crystal A is elongated from 13.1364Å to 13.2302Å. Figure 3 shows the room temperature X-ray diffraction (XRD) patterns for crystal A after oxidation. The lattice parameter c is close to the maximum value obtained in ceramic materials with T_c of 40K and/or 45K and δ-0.12.[3] This indicates that the crystal is highly oxidized and oxygen is believed to be inserted into the interstitial sites in the (La_2O_2) layers for the elongation of c-axis. But T_c in this crystal is low. It is known that T_c is influenced by hole concentration in the CuO_2 planes. We argue that the oxidation at 70°C can increase oxygen mobility and make oxygen ordering, i.e. oxygen clusters such as O_2^{2-} can be created. The interactions between the inserted oxygen ions reduce the doping efficiency because the oxygen ions accept less electrons when they form clusters. This is a possible reason for lower T_c of this crystal, compared with other high T_c phases when δ is close to each other.

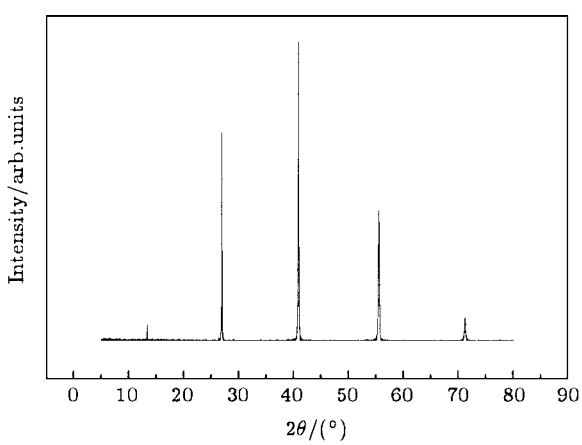


Fig.3. Room temperature XRD patterns for oxidized crystal A.

For room temperature oxidation on crystal B, even for much longer intercalating time of 2 months, oxidation is less effective compared with crystal A. Figure 4 (a) shows the magnetic susceptibility as a function of temperature in an applied high field H=0.3T for crystal B before oxidation. The paramagnetic behavior (χ/T^{-1}) is observed when temperature

T is below 300K and a frozen-oxygen peak at T-50K can also be seen. No AF ordering is found in this temperature region, indicating that the as-grown crystal B contains a few excess oxygen content. After oxidation, holes are doped into the CuO_2 planes and macroscopic phase separation has occurred. As shown in Fig.4 (b), a broad AF peak at the Néel temperature T_N=245K is observed in the magnetic susceptibility curve at an applied field H=0.5T. When T <200K, the behavior remains paramagnetic. Because the superconducting fraction is small, the applied field is larger than the upper critical field Hc_2 of the crystal and the sample is in normal state even at T <5K.

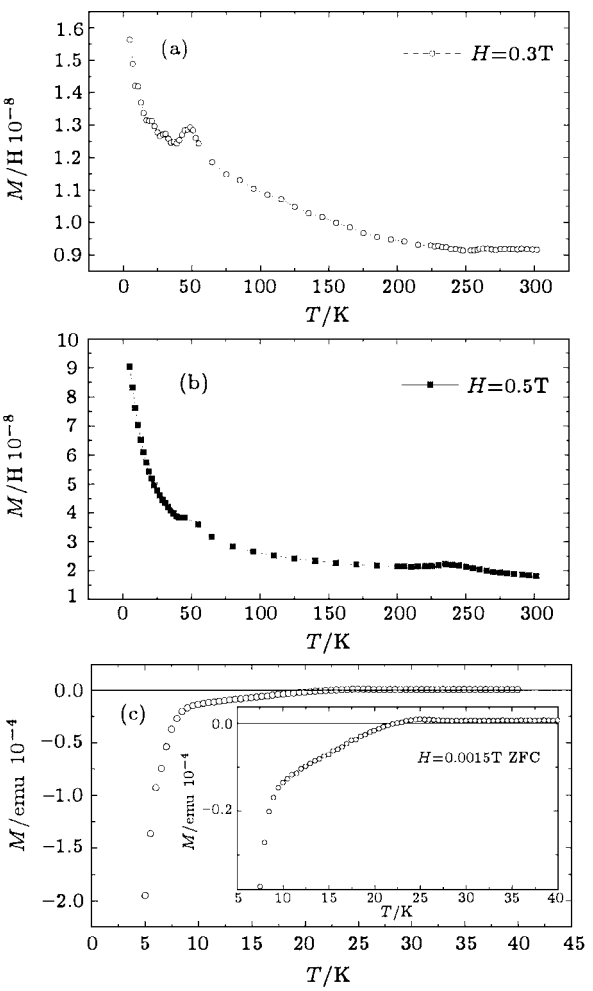


Fig.4. (a) Temperature dependence of magnetic susceptibility for crystal B before oxidation in field H=0.3T (b) Temperature dependence of magnetic susceptibility for crystal B after oxidation in field H=0.5T (c) Temperature dependence of magnetization for crystal B after oxidation in low field H=0.0015T. Data are measured in ZFC mode.

Figure 4(c) shows the temperature dependence of magnetization measured in ZFC mode with low field H=0.0015 T. There are two diamagnetic transitions at T_{c1}-24K and T_{c2}-8K, respectively. By comparison of the diamagnetism at 5K for crystal A and crystal B, it is found that the shielding signal is much smaller in crystal B. The inset in Fig.4 (c) shows the enlarged curve for crystal B, in which two superconducting transitions can be seen clearly.

The presence of AF ordering at T_N ~245K and superconducting transition at T_{c1}~24K indicates that crystal B is macroscopically phase-separated. The electrochemical treatment at room temperature produces an inhomogeneous distribution of intercalated O^{2-} ions. For the low oxygen-ion diffusion rate at room temperature, a high density of the excess oxygen is formed on the surface of the crystal, which is responsible for the phase separation. However, that the appearance of T_{c2} ~8K in the same crystal is due to the lightly doped inner part of the crystal. The cause of this low T_c phase is possibly the same as the one reported in Ref.[16], which is for the formation of non-segregated superconducting phase.

There are three phases coexisting in oxidized crystal B. Phase separation has occurred at room temperature, which can be confirmed by XRD pattern.For brevity we name the phase-separated oxygen-poor AF phase as phase 1, the oxygen-rich superconducting phase with T_{c1} of 24K as phase 2 and the non-separated superconducting phase with T_{c2} of 8K as phase 3.

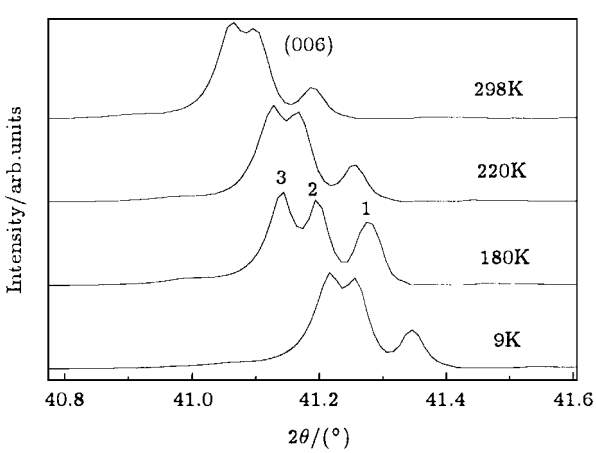


Fig.5. X-ray diffraction scans of the (006) Bragg reflections of crystal B at temperatures T=9K, T=180K, T=220K and T=298K

Figure 5 shows the portion of c-axis low-temperature XRD patterns for crystal B. The scans of

(006) Bragg reflections for a series of temperatures are shown in Fig.5. In agreement with the magnetization measurements in Fig.4, three phases can be distinguished from (006) reflection at room temperature; this means that phase-separation has occurred at room temperature. When temperature decreases to 180K, because the thermal expansion coefficients of the three phases are obviously different at this temperature, the difference among c-axis lengths of the three phases is shown from the (006) reflection. The temperature dependence of the c lattice parameter for the three phases is shown in Fig.6. When temperature decreases, the c-axis of each phase decreases almost linearly.

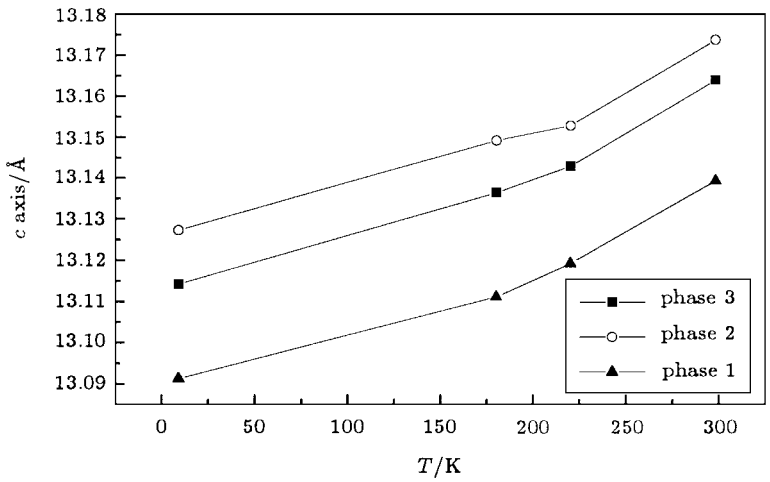


Fig.6. Temperature dependence of c lattice parameter for phase1, phase 2 and phase 3 in oxidized crystal B.

In conclusion, we have successfully oxidized the La_2CuO_4 single crystals by electrochemical oxidation. It is shown that electrochemical treatment at 70°C can produce a superconducting single phase with T_c 19K and oxygen content δ close to ~0.12. Oxidation at room temperature is inhomogeneous, as a result there are two superconducting phases with T_c's of 24 and 8K coexisting with one AF phase in the crystal. The appearance of T_c in $La_2CuO_{4+\delta}$ system is interesting, since single crystals of T_c=8, 12 and 24K have been observed in this work and Ref.[16]; for ceramic materials, T_c's of 15, 30 and 45K have also been observed.[8] The phase diagram of T_c versus hole concentration in this system does not obey the conventional parabolic "bell-jar" relationship; the appearance of T_c shows the "step" tendency. This kind of "step" tendency has also been found in Bi-2201 system[18], indicating that the intrinsic physical mechanism for high T_c superconductors needs further investigation.

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REFERENCES

[1] J. E. Schirber, B. Morosin, R. M. Merrill *et al., Physica,* **C152**(1988),121.
[2] E. Takayama-Muromachi and A. Navrotsky, *Physica,* **C218**(1993),164.
[3] A. Wattiaux, J. C. Park, J. C. Grenier *et al., C. R. Acad. Sci. Paris,* **310**(1990),1047.
[4] H. Sata, M. Naito, H. Yamamoto, *Physica,* **C280**(1997), 178.
[5] B. O. Wells, Y. S. Lee, M. A. Kastner *et al., Science,***277** (1997),1067.
[6] D. P. Scarfe, X. Z. Xiong, W. J. Zhu *et al., J. Mater. Res.,* **14**(1999),1221.
[7] X. Xiong, P. Wochner, S. C. Moss *et al., Phys, Rev. Lett.,* **76**(1996),2997.
[8] H. H. Feng, Z. G. Li and P. H. Hor *et al., Phys, Rev.,* **B51**(1995),16499.
[9] F. C. Chou, D. C. Johnston, S. W. Cheng, *et al., Physica* **C216**(1993),66.
[10] S-W. Cheong, Z. Fisk, J. O. Willis *et al., Solid State Commun.,* **65**(1988),111.

[11] J. C. Grenier, A. Wattiaux, N. Lagueyte *et al., Physica* **C173**(1991),139.
[12] B. Raveau, C. Michel, M. Hervieu *et al.,* Crystal Chemistry of High-T_c Superconductivity Copper Oxides, (Springer Series in Materials Science 15, Springer, Berlin, 1991).
[13] R. D. Sanchez, R. M. Torresi, C. Rettori *et al., Electrochimica Acta,* **40**(1995),209.
[14] E. Magnone, G. Cerisola, M. Ferretti *et al., J. Solid State Chem.,* **144**(1999),8.
[15] H. H. Feng, Ph. D. Thesis, University of Houston, USA, 1996.
[16] A. A. Zakharov, A. A. Nikonov and O. E. Parfionov, *Phys. Rev.,* **B57**(1998),R3233.
[17] F. Arrouy, J-P. Locuquet, E. J. Williams *et al., Phys, Rev.,* **B54**(1996),7512.
[18] W. L. Yang, H. H. Wen and Z. X. Zhao, (in preparation).