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Calorimetric study of an electrochemically oxidized crystal of $La_2CuO_{4.05}$: Stabilization phenomenon, phase transitions, and a glass transition due to freezing-in of the rearrangement of excess oxygen atoms

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Heat capacities of a $La_2CuO_{4.05}$ crystal prepared by electrochemical oxidation at room temperature were measured in the range of 14–400 K with an adiabatic calorimeter. The as-prepared sample exhibited heat evolution, above 330 K, due to stabilization from a metastable phase to a stable phase and to homogenization of the excess oxygen atoms over the whole polycrystalline sample. There were two phase transitions observed only for the stabilized sample; a Martensitic type at 290 K, and a second-order type at 158 K. A superconducting phase transition was observed near 41 K for both the as-prepared and the stabilized sample. A glass transition was found in the range of 130–190 K, and was interpreted to have originated from the freezing-in of the short-range rearrangement of excess oxygen atoms. Herein, the relationship between the phase transitions due to the order and/or disorder of excess oxygen atoms and to the tilt of the CuO_6 octahedra is discussed. [S0163-1829(99)09933-6]

I. INTRODUCTION

The structure of La_2NiO_4 and La_2CuO_4 crystals is the same as that of K_2NiF_4 constructed of alternatingly stacked $KNiF_3$ perovskite and KF rocksalt layers. Both the crystals show excess-oxygen nonstoichiometry, and the excess oxygen atoms are accommodated at interstitial sites surrounded by four lanthanum atoms and four oxygen atoms in LaO rocksalt layers.[1,2] Based on the fact that more excess oxygen δ can be incorporated in La_2NiO_4 crystals than in La_2CuO_4 crystals, studies of the δ-T phase relation and the ordered structure of excess oxygen atoms have conventionally employed the $La_2NiO_{4+\delta}$ crystals.[3–8] Notably, however, $La_2CuO_{4+\delta}$ crystals with large δ have been prepared by using an electrochemical oxidation technique.[9,10]

The presence of ordered structures of excess oxygen atoms in $La_2NiO_{4+\delta}$ crystals has been reported by several research groups, respectively,[3–7] using neutron-diffraction, electron-diffraction, and transmission electron microscopy techniques. Tranquada *el al.*,[6] by using neutron diffraction of $La_2NiO_{4+\delta}$ crystals, observed superlattice peaks with a modulation wave vector $(0,1,1/m)$ below approximate room temperature, and suggested that the appearance of the superlattice peaks are due to an order-disorder phase transition of excess oxygen atoms, in conjunction with the cooperative tilt of NiO_6 octahedra. The ordered arrangement of excess oxygen atoms as correspondent to the modulation wave vector $(0,1,1/m)$ is called a stage-m structure; stage-3 and stage-2 structures appear around $\delta \approx 0.07$ and $\delta \approx 0.10$, respectively, and phase separation occurs in the range between the two δ values. In the stage-m structure, the excess oxygen atoms are accommodated at the interstitial sites located within every m LaO layer along the c axis. According to the characteristic tilt pattern of the NiO_6 octahedra, only the alternate interstitial sites along the b axis and all the interstitial sites along the a axis appear to be accessible in the relevant LaO layer to the excess oxygen atoms. Our calorimetric study[11] confirmed, based on the transition entropies, the phase transitions are, in fact, of a type involving an order-disorder process of the excess oxygen atoms. $La_2CuO_{4+\delta}$ crystals with large δ prepared by electrochemical oxidation have also been reported to show the ordered structure of excess oxygen atoms and the phase transitions.[12–15] Wells *et al.*,[13,14] by investigating neutron diffraction of $La_2CuO_{4+\delta}$ single-crystal oxidized electrochemically, observed superlattice peaks with the modulation wave vector $(0,1,1/m)$ below room temperature which corresponds to stage-m structure.[6] In that investigation, the relation betweem m and δ remained unclear because, owing to the small size of the crystals, their δ values could not be determined. There is no direct evidence that excess oxygen atoms really undergo rearrangement to an ordered state at the specific temperature at which the superlattice peaks appear. The neutron-diffraction experiment is considered to have detected there only the development of a cooperative tilt pattern of the CuO_6 octahedra. Lanzara *et al.*,[15] using in-plane-polarized Cu K-edge extended x-ray absorption fine structure, observed that two kinds of planar Cu-O bond lengths appear below 150 K in an electrochemically oxidized crystal of $La_2CuO_{4.1}$, which indicates the presence of another phase transition.

It has been reported that excess oxygen atoms in $La_2CuO_{4+\delta}$ and in $La_2NiO_{4+\delta}$ crystals are mobile below room temperature.[16–19] In the heat-capacity measurements of a $La_2NiO_{4.094}$ crystal,[19] we observed a glass transition phenomenon due to the freezing-in of the rearrangement of excess oxygen atoms around 200 K. However, we did not observe a glass transition in previous heat-capacity measurements of $La_2CuO_{4.035}$ and $La_2CuO_{4.011}$ crystals,[20,21] possibly due to a small quantity of excess oxygen atoms. It is expected that such a glass transition would be observable in $La_2CuO_{4+\delta}$ crystals in which a larger quantity of excess oxygen atoms were introduced by means of electrochemical oxidation, as was the case in the $La_2NiO_{4.094}$ crystal.

In the present study, heat capacities of an electrochemically oxidized crystal of $La_2CuO_{4.05}$ were measured with an adiabatic calorimeter in the range of 14–400 K in order to clarify the phase relation and dynamic properties of excess oxygen atoms. The as-prepared sample exhibited a large heat evolution, above 330 K, due to the change from a metastable to a stable phase. It is suggested that the origin of the stabilization is the transformation that results in the ordered structure of excess oxygen atoms, and the homogenization of excess oxygen atoms across the grain boundary. Two phase transitions were observed for the stabilized sample; a Martensitic type at 290 K and a second-order type at 158 K. Neither transition has been indicated to accompany an order-disorder process of excess oxygen atoms. A freezing-in phenomenon of the rearrangement of excess oxygen atoms was observed in the range of 130–190 K.

II. EXPERIMENT

Details of the synthesis of a polycrystalline sample by electrochemical oxidation are described elsewhere.[22] The excess oxygen atom content δ of the sample was determined to be 0.05 by iodometric titration with an uncertainty of ± 0.01 after the heat capacity measurements. Heat capacities of the sample were measured in the range of 14–400 K by an intermittent heating method using a high-precision adiabatic calorimeter.[23] The initial temperature T_i is determined by following the temperature of a calorimeter cell for 12 min. A known quantity of electrical energy ΔE is then supplied to the calorimeter cell loaded with the sample, and the final temperature T_f is determined by following the temperature for another 12 min. Gross heat capacity of the cell C_total is evaluated to be $\Delta E/(T_\mathrm{f}-T_\mathrm{i})$ at $T_\mathrm{av}=(T_\mathrm{f}+T_\mathrm{i})/2$. Appreciable temperature drifts were observed during the temperature-measurement periods as due to a glass transition or a phase stabilization. The rates of the drifts were determined to be the values at 7 min after the supply of electrical energy. The mass of the sample used was 21.217 g (0.052239 mol). The precision and accuracy of the measurements were estimated to be within ± 0.06 and $\pm 0.3\%$, respectively.[23]

III. RESULTS

A. Phase relation

Figure 1 shows the rates of temperature drifts observed as originating from the change of state of the sample in the range of 300–400 K. Squares represent the values obtained upon heating the sample that had been prepared by electrochemical oxidation at room temperature. The sample exhibited heat evolution starting at around 330 K. Circles represent values obtained on heating the sample after annealing at 400 K for 60 h. The annealed sample exhibited no heat evolution nor heat absorption in the range of 300–400 K. Based on this finding, it is concluded that the heat evolution observed in the as-prepared sample is due to a kind of stabilization. Figure 2 shows the temperature drift observed near 400 K immediately after the series of heat-capacity measurements of the as-prepared sample had been carried out from 300 to 400 K. The temperature change ΔT due to the stabilization amounts to ~ 1.7 K. The magnitude of heat evolution, ΔH_m, is evaluated as the sum of two contributions as follows. The first contribution is estimated from heat evolution observed during the heat-capacity measurements from 300 to 400 K to be

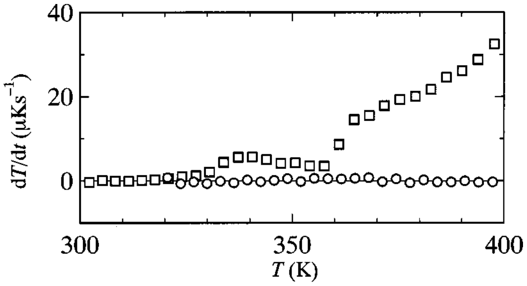

FIG. 1. Rates of spontaneous temperature drifts observed in the heat capacity measurements of a $La_2CuO_{4.05}$ crystal: □ is the as-prepared sample; ○ is the sample annealed at 400 K for 60 h.

$$\Delta H_{\mathrm{m},1}=\int C_\mathrm{total}/n(dT/dt)dt\approx 0.2\ \mathrm{kJ\,mol^{-1}}, \tag{1}$$

where C_total and n are the gross heat capacity and the quantity of sample, respectively. The second contribution is estimated from the heat evolution observed during the annealing at 400 K to be

$$\Delta H_{\mathrm{m},2}=C_\mathrm{total}(400\ \mathrm{K})\Delta T/n\approx 0.9\ \mathrm{kJ\,mol^{-1}}. \tag{2}$$

The total enthalpy change is thus estimated to be $\Delta H_\mathrm{m}=\Delta H_{\mathrm{m},1}+\Delta H_{\mathrm{m},2}\approx 1.1\ \mathrm{kJ\,mol^{-1}}$.

Squares and circles in Fig. 3 represent molar heat capacities of the as-prepared and stabilized samples, respectively. Both the as-prepared and stabilized samples showed a heat-capacity anomaly due to a superconducting phase transition near 41 K. Only the latter sample showed two additional heat-capacity anomalies: one was a Martensitic phase transition near 290 K; the other, a second-order phase transition near 158 K.

Figure 4 shows the heat capacities of the stabilized sample in the range of 260–300 K on an enlarged scale. The different symbols in the figure represent the values obtained on heating the samples that had been precooled from 320 K to the temperatures, respectively, indicated in the figure. The

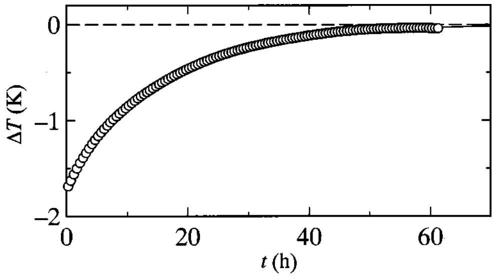

FIG. 2. Temperature drift curve at 400 K observed immediately after the heat capacities for the as-prepared sample had been measured from 300 to 400 K.

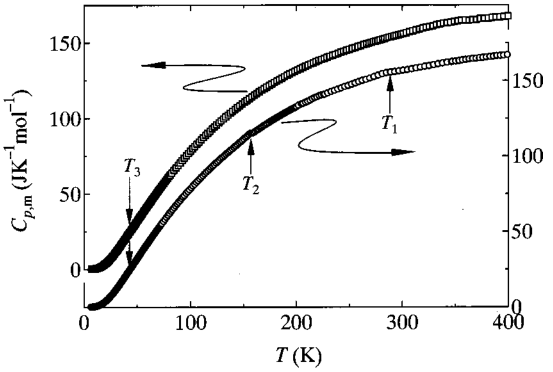

FIG. 3. Molar heat capacities of a $La_2CuO_{4.05}$ crystal: □ is the as-prepared sample; ○ is the sample annealed at 400 K for 60 h.

respective sets of data are located on different curves, as indicated by solid guidelines, depending on the lowest temperature to which the sample was precooled before the measurements. No appreciable temperature drift was observed just after the precooling or during the heat capacity measurements. These results indicate that the transformation pauses at a certain state of quasiequilibrium prefigured by the precooling temperature and cannot proceed due to the inevitable generation of large interfacial energy between the domains of high- and low-temperature phases. This is characteristic of a Martensitic phase transition, and is similar to those observed in $La_2CuO_{4.011}$ and $La_2CuO_{4.035}$ crystals.[20,21] The dashed line in the figure represents a baseline established by interpolating the values in the ranges of 200–250 K and 300–320 K. The baseline represents

$$C_{p,\mathrm{m}}/(\mathrm{JK^{-1}mol^{-1}}) = 22.12 + 0.7991(T/\mathrm{K}) - 1.337\times10^{-3}(T/\mathrm{K})^2 + 5.554\times10^{-7}(T/\mathrm{K})^3. \qquad (3)$$

The assumption that, above 300 K, there is no heat-capacity contribution due to the phase transition is consistent with the report by a neutron-diffraction experiment[13,14] that no appreciable signal of short-range order in the tilt of CuO_6 octahedra or in the arrangement of excess oxygen atoms has been observed at the temperatures in $La_2CuO_{4+\delta}$ crystals. The enthalpy and the entropy of transition were estimated by setting the baseline to be 24 J mol^{-1} and 0.096 J K^{-1} mol^{-1}, respectively.

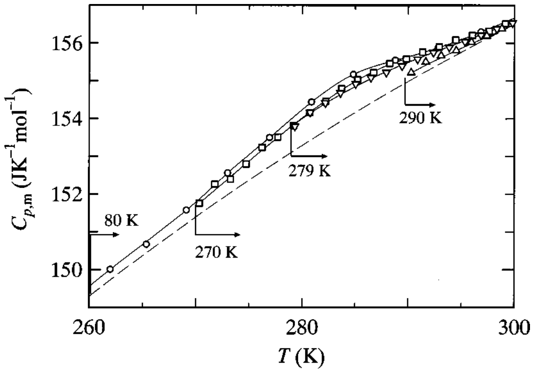

FIG. 4. Molar heat capacities plotted on an enlarged scale near 290 K. Temperatures indicated in the figure represent the lowest temperatures to which the samples were precooled from 320 K before each series of measurements. Dashed line represents a base line for estimation of the enthalpy and entropy of transition. Solid lines are guide for eyes.

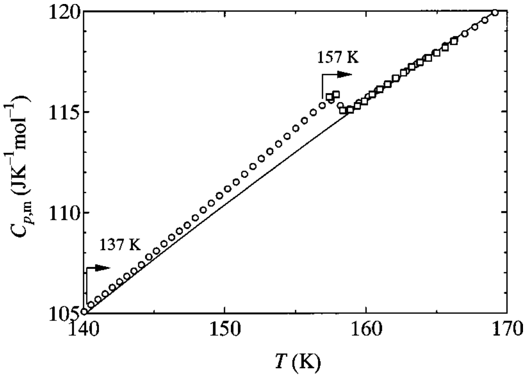

FIG. 5. Molar heat capacities plotted on an enlarged scale near 158 K. Temperatures indicated in the figure represent the lowest temperatures to which the samples were precooled from 200 K before each series of measurements. Solid line represents a base line for estimation of the enthalpy and entropy of transition.

Figure 5 shows the heat capacities of the stabilized sample in the range of 140–170 K on an enlarged scale, and the two symbols represent values obtained on heating samples precooled from 200 K to the temperatures (137 and 157 K, respectively) indicated. The two sets of data are located on the same curve independent of the lowest temperature to which the sample was precooled, and no temperature drift was observed during the measurements. This indicates the absence of hysteresis and latent heat in the transition. The anomalous heat-capacity curve showed a long tail on the low-temperature side and an abrupt drop just above the transition temperature. These figures further indicate that the phase transition is of a second order. The solid line in the figure stands for a baseline established by interpolating the values in the ranges of 50–100 K and 165–180 K. The line represents

$$C_{p,\mathrm{m}}/(\mathrm{JK^{-1}mol^{-1}}) = -29.38 + 1.502(T/\mathrm{K}) - 1.035\times10^{-2}(T/\mathrm{K})^2 + 1.548\times10^{-4}(T/\mathrm{K})^3 - 1.500\times10^{-6}(T/\mathrm{K})^4 + 6.790\times10^{-9}(T/\mathrm{K})^5 - 1.152\times10^{-11}(T/\mathrm{K})^6. \qquad (4)$$

The enthalpy and the entropy of transition were estimated by setting the baseline to be 15 J mol^{-1} and 0.10 J K^{-1} mol^{-1}, respectively. Considering that the value of the entropy is small, the transition is indicated to be based on a small displacement of ions. This is consistent with the fact that the excess oxygen atoms are immobile in the phase-transition temperature region as described in the next section.

In order to estimate the magnitude of the heat-capacity jump, $\Delta_{\mathrm{trs}}C_{p,\mathrm{m}}$, associated with the superconducting phase transition, excess heat capacities, $\Delta C_{p,\mathrm{m}}$, were calculated by subtracting the heat capacities of a $La_2CuO_{4.00}$ crystal[20] from the observed values. Squares and circles in Fig. 6 represent $\Delta_{\mathrm{trs}}C_{p,\mathrm{m}}/T$, the excess heat capacities divided by tempera-

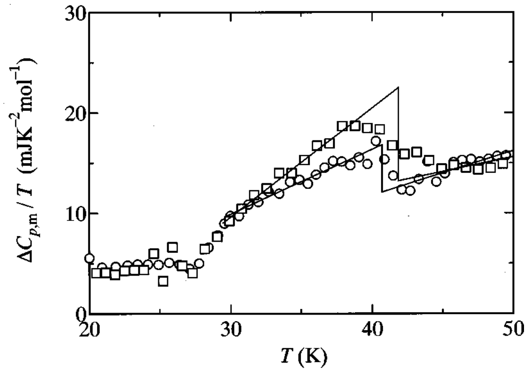

FIG. 6. Excess molar heat capacities divided by temperature of $La_2CuO_{4.05}$ crystal, derived by subtracting the values of a $La_2CuO_{4.00}$ crystal from the experimental ones and plotted on an enlarged scale near 41 K: □ is the as-prepared sample; ○ is the sample annealed at 400 K for 60 h. Solid lines are guide for eyes.

ture, for the as-prepared and stabilized samples, respectively, in the range of 20–50 K. The superconducting phase transition was observed to have a jump at around 41 K in both samples. The magnitude of the jump is estimated to be 10 and 5 $\mathrm{mJ\,K^{-2}mol^{-1}}$ for the as-prepared and stabilized samples, respectively. These values are similar to those, 1.73–7.67 $\mathrm{mJ\,K^{-2}\,mol^{-1}}$, of $La_{2-x}Sr_xCuO_4$ $(0.10 \leqslant x \leqslant 0.16)$ crystals.[24]

B. Glass transition due to freezing-in of rearrangement of excess oxygen atoms and activation energy for the positional jump of the oxygen atom

Solid and open circles in Fig. 7 show the rates of temperature drifts observed in two series of measurements for samples stabilized at 400 K and subjected to respective precooling treatment at 1 $\mathrm{K\,min^{-1}}$ and at 20 $\mathrm{mK\,min^{-1}}$ from 200 to 100 K. The rapidly precooled sample exhibited heat evolution starting at 130 K and ending near 190 K. The slowly precooled sample exhibited heat absorption starting at 145 K and ending near 190 K. The heat evolution and heat absorption are not associated with the phase transition at 158 K, because the temperature, 170 K, of the heat absorption peak is clearly separated from the transition temperature. The fact that the heat evolution observed in the rapidly precooled sample changes to heat absorption in the slowly precooled sample leads to the conclusion that the effects of heat evolution and absorption are due to a glass transition. The glass transition temperature, T_{g}, at which the relaxation time is 10^3s, was determined from an empirical relation[23] to be 170 K, at which the slowly precooled sample exhibited a heat absorption peak. Such a glass transition was also observed in a $La_2NiO_{4.094}$ crystal, and is understood to be caused by the freezing-in of the rearrangement of excess oxygen atoms.[19]

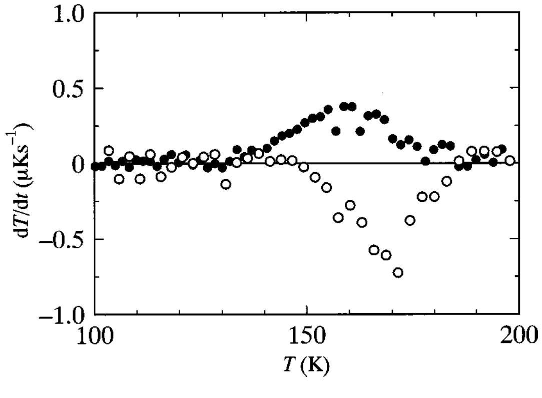

FIG. 7. Rates of temperature drifts observed in the series of heat capacity measurements for the $La_2CuO_{4.05}$ crystal stabilized at 400 K: ● is the sample precooled rapidly at 1 $\mathrm{K\,min^{-1}}$; ○ is the sample precooled slowly at 20 $\mathrm{mK\,min^{-1}}$.

The activation energy, $\Delta\varepsilon_{\mathrm{a}}$, for the positional jump of an excess oxygen atom is estimated as follows. The relaxation time τ and frequency f for the jump are connected by the relation

$$f = 1/2\pi\tau. \tag{5}$$

The jump frequency is expressed by

$$f = \nu \exp(\Delta S_{\mathrm{a}}/R)\exp(-\Delta\varepsilon_{\mathrm{a}}/RT), \tag{6}$$

where ν, ΔS_{a}, and R are the vibrational frequency of excess oxygen atoms, activation entropy, and gas constant, respectively. Both of $\Delta\varepsilon_{\mathrm{a}}$ and ΔS_{a} are usually considered to be independent of temperature. ν is expected to be close to the Debye frequency, 1.02×10^{13} Hz, which was estimated from the molar heat capacity value at the glass transition temperature by assuming the crystal to be a continuous solid composed of $7.05\times N_{\mathrm{A}}$ atoms, where N_{A} is Avogadro's number. According to Zener theory,[25] ΔS_{a} can be estimated as

$$\Delta S_{\mathrm{a}} \approx -\Delta\varepsilon_{\mathrm{a}} \frac{d(B/B_0)}{dT}, \tag{7}$$

where B and B_0 are bulk moduli at T and 0 K, respectively. Based on bulk modulus data,[26] an average value of $d(B/B_0)/dT$ between 47 and 310 K is calculated to be $-4.21\times10^{-5}\ \mathrm{K^{-1}}$. Using these values of $d(B/B_0)/dT$ and ν, and given that the relaxation time at T_{g} is 10^3s, the activation energy, $\Delta\varepsilon_{\mathrm{a}}$, for the jump of the excess oxygen atom is estimated according to Eqs. (5)–(7) to be equal to 55.1 $\mathrm{kJ\,mol^{-1}}$, which is close to the value of 47 $\mathrm{kJ\,mol^{-1}}$ estimated by the measurements of elastic energy loss.[27] The relaxation time is determined by

$$\tau = \tau_0 \exp(\Delta\varepsilon_{\mathrm{a}}/RT) \tag{8}$$

with $\tau_0 = 1.18\times10^{-14}$s, which is close to the value of 2×10^{-14}s estimated by the measurements of elastic energy loss[27] and is in the range previously predicted.[28]

IV. DISCUSSION

A. Absence of an order-disorder process of excess oxygen atoms in the phase transition at around 290 K

In the present study, the phase transition observed at around 290 K was clearly related to the observation by Wells *et al.*[13,14] of superlattice peaks below room temperuture in electrochemically oxidized crystals. The superlattice peaks corresponded to a stage structure similar to those observed in $La_2NiO_{4+\delta}$ crystals.[6] It should be noted, however, that the superlattice peaks are not necessarily a result of the development of ordered arrangement of excess oxygen atoms, but are attributed to the development of the tilt pattern of CuO_6 octahedra. In a $La_2NiO_{4+\delta}$ crystal with $\delta \approx 0.07$,[11] the entropy of the staging transition was about 1 $J K^{-1} mol^{-1}$, and a large heat absorption effect, owing to diffusion of excess oxygen atoms over a broad expanse, was observed in the heat-capacity measurements around the transition temperature. On the other hand, in the $La_2CuO_{4.05}$ crystal, the entropy of the transition at around 290 K was found to be about 0.1 $J K^{-1} mol^{-1}$, only one tenth that found in $La_2NiO_{4.07}$, and no appreciable heat absorption effect was observed in the transition region. Judging from the results of calorimetric and neutron-diffraction studies,[13,14] it is concluded that an order-disorder process of excess oxygen atoms does not proceed but only the cooperative tilt of the CuO_6 octahedra occurs through the phase transition at around 290 K. Considering that the superlattice peaks observed in $La_2CuO_{4+\delta}$ ($\delta \geqslant 0.055$) crystals below room temperature are similar to those of the stage structure observed in $La_2NiO_{4+\delta}$ ($\delta \approx 0.07$ and 0.10) crystals, it is deduced that, for the $La_2CuO_{4.05}$ crystal, the excess oxygen atoms are ordered with stage structure at least in the phase below 290 K. Furthermore, in view of the fact that the ordering/disordering of excess oxygen atoms is not involved in the phase transition at 290 K, it follows that, in the $La_2CuO_{4.05}$ crystal, the excess oxygen atoms are already ordered in the phase above 290 K.

B. Two processes that proceed in the stabilization observed above 330 K in the as-prepared sample

Two processes are considered to proceed in the stabilization observed above 330 K in the as-prepared sample. One is the homogenization of the excess oxygen atom content in the sample in which the excess oxygen atoms were incorporated heterogeneously by electrochemical oxidation at room temperature. The other is a phase transition from a metastable to a stable phase, which results in a stage structure of excess oxygen atoms without tilt of CuO_6 octahedra in an ordered fashion. The former process was proposed by Hirayama *et al.*[29] In view of the fact that the glass transition caused by the freezing-out of the rearrangement of excess oxygen atoms was observed around 170 K, the excess oxygen atoms are understood to be mobile in a crystal above 170 K. The sample was, however, electrochemically oxidized in the form of polycrystals, and thus the homogenization of excess oxygen atom content over the whole sample requires diffusion of the oxygen atoms across the grain boundaries of the polycrystals. This process potentially proceeds only at high temperatures, such as those above 330 K. Hirayama *et al.* really reported that a $La_2CuO_{4+\delta}$ crystal prepared by electrochemical oxidation at room temperature showed two superconducting transitions, at $T_c = 45$ and 32 K, and that the transition at 45 K disappeared by annealing at 373 K. They interpreted this result to be associated with homogenization: *viz.*, the excess oxygen atoms are incorporated only in the surface region of the polycrystalline sample by electrochemical oxidation at room temperature, and diffuse into the inner part of the sample by means of the annealing at 373 K. In the present study, the heat-capacity jump induced at the superconducting phase transition was observed to decrease by annealing at 400 K, as shown in Fig. 6. This finding may be explained further by the progress of homogenization. The annealing is then understood to remove those crystals in the sample that have very large δ values, which would give comparatively large heat-capacity jumps.

The latter process can be predicted to proceed as follows in the stabilization that occurs above 330 K. Prior to electrochemical oxidation, the La_2CuO_4 crystal is in the phase with the space group of $Bmab$,[6] in which the CuO_6 octahedra are correspondingly tilted in a systematic way, though the tilt pattern is different from that realized in the low-temperature phase below 290 K in $La_2CuO_{4.05}$.[14] On the other hand, as discussed in the last section, the CuO_6 octahedra in the stable phase of $La_2CuO_{4.05}$ crystal above 290 K have no tilt at least in the long range.[14] This indicates that the samples before and after electrochemical oxidation at room temperature have different stable phases with different structures. If the phase transition between the two phases is of the first order, proceeding through the progress of the new-phase nucleation and growth processes, the progress requires adequate conditions in terms of temperature and time period. In this respect, the as-prepared sample is potentially in the metastable $Bmab$ phase but not in the stable phase. Notably, the structural phase transitions below room temperature were observed only in the stabilized sample, but not in the as-prepared sample. This finding is consistently interpreted based on the assumptions that the as-prepared crystals have structures rather close to those characteristic of the $Bmab$ phase in terms of the tilts of the CuO_6 octahedra, and result in no structural phase transition below 300 K, as in the case of the La_2CuO_4 crystal and, further, the phase transitions take place in the crystal with some ordered arrangement of excess oxygen atoms after the stabilization. It is unlikely that the stabilization yields only the above homogenization while giving the appearance of the phase transitions; if that were the case, the phase transitions would have been detected in the temperature range in the as-prepared sample, since such transitions are observed in $La_2CuO_{4+\delta}$ crystals not only with $\delta = 0.05$ but also with $\delta = 0.011$ and 0.035.[20,21] Crystals with these δ values are expected to exist in appreciable amounts even immediately after the electrochemical oxidation at room temperature. Thus, the stabilization above 330 K is concluded to include the phase transition resulting in the stage structure of excess oxygen atoms without the cooperative tilt of the CuO_6 octahedra. We remarked that no heat evolution was observed in the previous heat-capacity measurements of the $\delta = 0.011$ and 0.035 crystals prepared by high-pressure oxygen annealing above 400 K.[20,21] Since the heat evolution, i.e., stabilization process could proceed above room temperature, the $\delta = 0.011$ and 0.035 crystals would have undergone this transition during the high-temperature annealing.

C. Freezing-in of short-range rearrangement of excess oxygen atoms

It was found that the rearrangement motion of excess oxygen atoms is frozen-in near 170 K in a $La_2CuO_{4.05}$ crystal. The temperature, 130 K, at which heat evolution was observed to commence for the rapidly precooled sample is close to that, 150 K, for the $La_2NiO_{4.094}$ crystal.[19] The temperature region of the glass transition, 130–190 K, is, however, narrower than that of 150–300 K in the case of the $La_2NiO_{4.094}$ crystal. The glass transition in the latter case is associated with phase separation with respect to excess oxygen atom content; thus the oxygen atoms have to diffuse over long distances. Because the relaxation time for diffusion over a long distance becomes very long, the relaxation should be observed over a wide temperature region up to a high temperature, as discussed in a previous paper.[19] The fact that the temperature region of the present glass transition is rather narrow indicates that the glass transition in a $La_2CuO_{4.05}$ crystal is not associated with long-distance diffusion of excess oxygen atoms but is, rather, due to a freezing-in of the short-range rearrangement of excess oxygen atoms. The short-range ordering of the excess oxygen atoms within each layer of accessible sites can be a candidate for rearrangement mode.

V. CONCLUDING REMARKS

In the present study, it was found that the phase transition at around 290 K does not involve an order-disorder process of excess oxygen atoms but, rather, involves only a small displacement of ions. Further, the stabilization observed above 330 K accompanies the phase transition and results in a stage structure in the arrangement of the excess oxygen atoms without the cooperative tilt of the CuO_6 octahedra. This would indicate that an order-disorder transition of the excess oxygen atoms would take place above 400 K; that is, the fact that the ordering of excess oxygen atoms does not accompany the cooperative tilt of CuO_6 octahedra makes this case different from that of the $La_2NiO_{4+\delta}$ crystal. Of notable interest herein is the clarification of the coupling and/or decoupling mechanism between the cooperative ordering of excess oxygen atoms and the cooperative tilt of MO_6 ($M = \mathrm{Ni}$, Cu) octahedra.

The observation that the heat-capacity jump at the superconducting transition temperature is about half as large in the stabilized sample as in the as-prepared sample was understood as an effect of the homogenization of excess oxygen atoms over the whole sample. A real understanding of this phenomenon requires future study on the δ-T phase diagram and the δ dependence of the heat-capacity jump associated with the superconducting phase transition. In view of the findings that no heat-capacity jump was observed at $\delta = 0.011$ and 0.035, and in light of the fact that the above homogenization at the average $\delta \sim 0.05$ brought the jump to decrease much, further investigation promises interesting results.

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