Novel measuring and correction method of oxygen content in La$_{2-x}$Sr$_x$CuO$_y$ superconductors with the dissolved oxygen sensor

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It is known that Cu valence of cuprate superconductors govern transition temperature ($T_c$). For La$_{2-x}$Sr$_x$CuO$_y$ when $x = 0.15$, that is, $v$ is 2.15, the highest $T_c$ around 40 K is achieved. The $v$ value is determined both by strontium and oxygen content. So far, coulometry and iodometry have been used for determining oxygen content. However, chemical analysis usually requires much experience. The purpose of this research is to develop a novel measuring method of oxygen content in cuprate superconductors with a newly developed dissolved oxygen (DO) sensor and to discuss correction method. Signal received from the DO sensor is sent to PC automatically without any external power supply. Oxygen content obtained with DO sensor was compared with iodometry. It was found that this method is reliable enough to determine oxygen content in La$_{2-x}$Sr$_x$CuO$_y$, and is called dissolved oxygen (DO) method.

Key-words : DO sensor, Oxygen content, Cu valence

1. Introduction

It is well-known that oxygen content in copper based superconductors is an important factor for determining transition temperature ($T_c$). For La$_{2-x}$Sr$_x$CuO$_y$ (LSCO) superconductivity is seen in the composition range from $x = 0.06$ to 0.25. Cu valence, $v$, is calculated from Sr content, $x$ and oxygen content, $y$, by equation $v = x + 2y - 6$ in La$_{2-x}$Sr$_x$CuO$_y$. Since the oxygen content ($y$) of La$_{2-x}$Sr$_x$CuO$_y$ is $\sim$4, $v$ is calculated approximately by $x + 2$. Therefore, in La$_{2-x}$Sr$_x$CuO$_y$ samples, transition temperature ($T_c$) of La$_{2-x}$Sr$_x$CuO$_y$ increases with increasing Cu valence from $v = 2.0$ to 2.15.

In the past decades, various methods have been proposed for measuring oxygen content. The oxygen content measurement methods are listed in Table 1. As a conventional method, the Thermogravimetry (TG) was used to measure the weight loss of an oxide during controlled heating. However, even in the case that the material does not contain unstable elements such as Hg or Tl, the accuracy of the oxygen content observed by TG is less than that achievable by chemical analysis. By using Auger electron spectroscopy and photoelectron spectroscopy, oxygen content can be measured with the weight of 1 ug oxide. However, they are surface sensitive. Near the surface, oxide impurities such as carbonate or hydroxide are usually formed. To eliminate impurity effect, surface scraping under high vacuum is required. On the other hand, for chemical analysis, oxygen content is measured rather accurately. As an example, the iodometry method was used to determine the oxygen content of single-phase HgBa$_2$CuO$_4$.$x$. Furthermore, to improve the reliability of the measurement, several experiments are required, with the result that several hundred mg of a specimen is required in total. An improved coulometry method was found to yield the oxygen content of an YBa$_2$Cu$_3$O$_{7-\delta}$ reference sample with a reproducibility within ±0.01 for samples with a mass of ~10 mg.

In this research, we will propose quite a new oxygen content measurement method, that is, dissolved oxygen (DO) measuring method. Oxygen content calculated by the dissolved oxygen measuring method is compared with that calculated by the iodometric method. The correction in a dissolved oxygen measuring method is also discussed.

2. Experimental

2.1 Sample preparation

La$_{2-x}$Sr$_x$CuO$_y$ ($x = 0.00$, 0.025, 0.05, 0.075, 0.01, 0.0125, 0.015, 0.0175, and 0.02) were prepared (Fig. 1). As starting materials, La$_2$O$_3$, SrCO$_3$ and CuO with high purity (>99.99%) chemicals were used. The powders were calcined at 800°C for 10h in air and then naturally cooled. The powders were then pressed into pellets. They were sintered at temperature 1050°C for another 20h and naturally cooled in the furnace again. The specimens were identified by X-ray powder diffraction method. After the specimen was confirmed to be single-phase, oxygen content was measured by both iodometric and DO methods.

Fig. 1. Flow chart of sample La$_{2-x}$Sr$_x$CuO$_y$ composition.

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2.2 XRD

Single-phase of La\(_{2-x}\)Sr\(_{x}\)CuO\(_y\) was confirmed by X-ray powder diffraction with Cu K\(_\alpha\) radiation by using a RINT 2000 wide-angle goniometer at room temperature. The voltage and current were set to be 40 kV and 20 mA. The range of 2\(\theta\) and its sweep rate were 5\(^\circ\)–60\(^\circ\) and 4\(^\circ\)/min, respectively.

2.3 Oxygen measurement

2.3.1 Iodometric measurement

Cu valence and oxygen content of each specimen were determined by iodometric titration. 50 mg of the LSCO and KI powder was put in a beaker. 10 ml of HCL solution was powered into the beaker and mixed until the LSCO and KI powder was completely dissolved. 1 ml of starch solution was added to the solution, and it was titrated by 0.01 mol/L \(\text{Na}_2\text{S}_2\text{O}_3\) till the purple color disappeared.

2.3.2 DO method

Ar gas with a flow rate of 5 ml/min was flown in 1 mol/L aq. HCl. By using Ar bubbling, background of the dissolved oxygen content in aq. HCl is decreased. The change in temperature and atmosphere, drastically changes DO value. After 10 min, the value of dissolved oxygen was stabilized at 0–19.99 mg/L. The dissolved oxygen data is sent to PC every second, and the data is displayed and saved on PC. The dissolved oxygen is corrected automatically against temperature chloride ion concentration, and pressure.

The principle is as follows;

If metal oxide is dissolved in HCl, valence of metal is changed to a stable value. In case of copper, it is changed to 2\(+\);

\[
\text{CuO}_{1+z} + 2\text{H}^+ \rightarrow \text{Cu}^{2+} + \text{H}_2\text{O} + \frac{Z}{2} \text{O}_2^\uparrow. \tag{1}
\]

When copper valence of copper oxide is smaller than two, copper will react with dissolved \(\text{O}_2\);

\[
\text{CuO}_{1-z} + 2\text{H}^+ + \frac{Z}{2} \text{O}_2 \rightarrow \text{Cu}^{2+} + \text{H}_2\text{O}. \tag{2}
\]

The dissolved oxygen will vary with the change in Cu valence. Thus, oxygen content of oxide is calculated as follows;

\[
M_{\text{GdScO}_3} = \frac{m_5}{M_5}.
\]

\[
M_{\text{O}_2} = (\Delta eV \times 10^{-3})/32
\]

\[
l : z/2 = M_{\text{GdScO}_3} : M_{\text{O}_2} = (m_5/M_5) : [(\Delta eV \times 10^{-3})/32]
\]

\[
z = (\Delta eVM_5 \times 10^{-3} \times 2)/(M(MgM_5)) \tag{3}
\]

where \(M_{\text{GdScO}_3} \Delta e, V, M_{\text{O}_2}, m_5\) and \(M_5\) are molecular weight of LSCO, DO change (mg/L), volume of solution (L), molecular weight of \(\text{O}_2\), weight of specimen (g), and formula weight of the specimen, respectively.

### Table 1. Oxygen content measurement

| Type          | Method                              | Weight of sample | Accuracy | Time | Merit                        | Demerit                              |
|---------------|-------------------------------------|------------------|----------|------|------------------------------|--------------------------------------|
| Physical      | Thermal gravity analysis            | 0.1 mg           | 0.1%     | 1 h  | High accuracy                | Absolute oxygen content measurement is impossible. |
| analysis      | Oxygen analyzer                     | 1 g              | 10%      | 10 min | The measurement is easy.     | Much sample is needed. Low accuracy | Surface sensitive |
| Auger electron spectroscopy (AES) | 1 \(\mu\)g | 10% | 1 h | Depth profile can be measured. | Surface sensitive |
| Photoelectron spectroscopy (XPS)     | 1 \(\mu\)g | 10% | 1 h | Depth profile can be measured. | Surface sensitive |
| Chemical      | Coulometry                          | 50 mg            | 0.1%     | 1 h  | High accuracyAutomatic measurement is possible. | Much time is needed. |
| analysis      | Iodometry                           | 50 mg            | 0.1%     | 1 h  | The error is small.          | Much time is needed. |

Fig. 2. The schematic view of DO method.
3. Results and discussion

3.1 XRD results

In Fig. 3, XRD patterns of La$_{2-x}$Sr$_x$CuO$_y$ (0.00 ≤ x ≤ 0.2) are shown. It is found that peaks observed by 0 ≤ x ≤ 0.2 are observed and that no impurity peaks are assigned. The XRD patterns of prepared LSCO’s (0 ≤ x ≤ 0.2) fit that of single-phase LSCO, indicating that the prepared specimens are all single-phase. It is to be noted that the (110) peak of the patterns in the range of 0 ≤ x ≤ 0.025 separates into two peaks, which is explained by the orthorhombic distortion from tetragonal phase.10)

3.2 Iodometric method

In Table 2, Cu valence (v) and oxygen content (y) of La$_{2-x}$Sr$_x$CuO$_y$ (x = 0.0–0.2) together with calculated v and y are listed. Oxygen content (y) was calculated by $y = (v + 6 - x)/2$. Iodometry data show that y is 4 ± 0.02 (x = 0.0–0.2), which roughly agree with the assumption of $y \sim 4.0$.1

3.3 Dissolved oxygen (DO) method

In Fig. 4, change of dissolved oxygen concentration against time is shown. The weight of LSCO is fixed at 50 mg and the content of hydrochloric acid solution for dissolving is varied from 10 to 500 ml. After putting LSCO into the solution (t = 0), dissolved oxygen content increases for 50 s. The dissolved oxygen in solution goes out to the atmosphere, the oxygen concentration decreases slowly. The difference (Δc) between maximum DO value and the DO value when t = 0 was measured. From the change of DO and volume of solution, the content of dissolved O$_2$ is measured, resulting that Cu value (v) and oxygen content (y) are calculated by Eq. (3). It is to be noted that Δc seems underestimated because the DO value takes time to dissolve oxygen in the solution, while escape oxygen into air starts from t = 0.

In Table 3, dependences of oxygen content and Cu valence of La$_{1.85}$Sr$_{0.15}$CuO$_y$ by DO method on the content of hydrochloric acid solution are listed. As shown in Fig. 4, as the solution

### Table 2. Table of Cu valence and oxygen content of La$_{2-x}$Sr$_x$CuO$_y$

| Sr content, x in La$_{2-x}$Sr$_x$CuO$_y$ | Iodometry | Cu valence (v) | Oxygen content (y) |
|----------------------------------------|-----------|----------------|-------------------|
| 0                                      | 1.994     | 3.997          |
| 0.025                                  | 2.046     | 4.011          |
| 0.05                                   | 2.083     | 4.017          |
| 0.075                                  | 2.096     | 4.011          |
| 0.1                                    | 2.130     | 4.015          |
| 0.125                                  | 2.136     | 4.006          |
| 0.15                                   | 2.160     | 4.005          |
| 0.175                                  | 2.179     | 4.002          |
| 0.2                                    | 2.220     | 4.010          |

Fig. 3. XRD patterns of La$_{2-x}$Sr$_x$CuO$_y$.

Fig. 4. Time dependence of dissolved oxygen concentration when the solution volume, V (ml) was changed. (La$_{1.85}$Sr$_{0.15}$CuO$_y$)
volume ($V$) becomes larger, the variation in the DO concentration ($c$) becomes smaller. Smaller $V$ results in the oxygen released to the atmosphere faster. And more oxygen left from LSCO slower is measured by the DO sensor, resulting that the oxygen content increases from 3.954 to 3.981 as the solution volume increases from 10 to 500 ml. So the content of hydrochloric acid solution becomes larger from 10 to 500 ml, oxygen content becomes larger and approaches to 4.00.

In Fig. 5, $v$ and $y$ of LSCO ($x = 0.15$) vs. volume of aq. HCl, $V$ (ml). The dependence of dissolved oxygen concentration on time is shown, indicating that DO's concentration increase rapidly just after adding the LSCO specimens at 0 set. The increase in DO concentration comes from the release of oxygen shown in Eq. (1). From the peak height ($c$) of DO from the background level, excess oxygen, $z$ is obtained from Eq. (3). Background of $c$ varies by temperature. Since the background is constant under the same temperature, it is therefore subtracted accurately in each experiment.

In Table 4, Cu valence ($v$) and oxygen content ($y$) of La$_{2-x}$Sr$_x$CuO$_y$ together with calculated $v$ and $y$ are listed. While $v$ obtained by iodometry is between 1.994–2.22, that obtained by DO is between 2.009–2.16, indicating that those $v$ and $y$ by DO method are smaller than those by iodometric method.

In Fig. 7, dependence of $v$ of LSCO on $x$ is shown. It is known that $v$ increases with an increase in $x$, which is consistent with the plots of iodometric and DO method. The Figs. 7(a) and 7(b) represent the data of (a) before correction and (b) after correction, respectively. The $v$ values obtained by DO method are 0–0.1 smaller compared to those obtained by iodometric method.

3.4 Multiplication correction
From Fig. 7(a), it is found that the $v$ values measured by DO method are smaller than those by iodometry. The difference becomes larger as $x$ increases from 0 to 0.2, indicating that we think that some portion of oxygen is trapped by the DO sensor. In order to agree the Cu valence calculated by DO method with that calculated by iodometry, if 42% of oxygen is not trapped by the DO sensor, corrected oxygen content is calculated by multiplying $\Delta c$ by 1.71 in Eq. (3).
Fig. 6. Dependence of dissolved oxygen concentration on time.

Fig. 7. Relation between Sr content, $x$ and Cu valences by iodometry and DO methods.
Figure 7(b) shows the results of Cu valence with iodometric method and dissolved oxygen method after correction. After correction, the difference is as small as 0.02 on the average, and is reduced to 0.06 at maximum.

It is found that multiplication correction method is very useful for estimating \( v \) and \( y \), but the multiplication coefficient may change with different measuring condition. Since we don’t try this experiment for other oxides, we don’t know whether this value is applicable for other oxides. In order to speculate the discharged oxygen from the specimen more precisely, better correction method is now under consideration.

4. Conclusion

By using newly developed DO sensor, novel measuring method of oxygen content in LSCO superconductors was found, which is called DO method, was established. The optimum volume of aq. HCl solution was found to be 100 ml. Cu value (\( v \)) and oxygen content (\( y \)) measured by DO method were compared with those by iodometry. The \( v \) and \( y \) values measured by DO method were 0–0.10 and 0–0.05 smaller than those by iodometry, respectively. The difference may come from degas of O\(_2\) from the solution to the air during dissolution. But in this paper, we don’t take the effect into account. The correction is under consideration and will be done in the next paper. In order to correct the \( v \) and \( y \) values, it was assumed that 58% of oxygen is trapped by the DO sensor. After correction, difference of \( v \) was reduced to 0.06 at maximum, indicating that DO method is very useful for determining \( v \) and \( y \) of LSCO. By using our proposed method, the amount of sample in experiment can be decreased less than 50 mg and the experiment period can be shortened for 15 min. This method will be applied for not only oxide superconductors but other ceramics. The decrease of the amount of sample will be tried in the near future. In order to speculate the discharged oxygen more precisely, new correction method is under consideration.

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