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Oxygen Measurement in Cuprate Superconductors Using the Dissolved Oxygen/Chlorine Method

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Abstract: We have developed a dissolved oxygen (DO) method with differential equation (DE) correction. We measured the oxygen content in La-based and Y-based superconductors, and succeeded in measuring the oxygen content simply in one-third of the time required by the iodometric titration method. However, there was a problem with Bi-based superconductors where the measured oxygen content was smaller compared to the iodometric titration method. We hypothesized that not only O₂ but also Cl₂ gas is generated when dissolving Bi-based superconductors and developed a dissolved oxygen/chlorine (DO/Cl) method with DE correction. This method uses only a dissolved oxygen sensor and a dissolved chlorine sensor to measure the dissolved oxygen and dissolved chlorine content in Bi₂Sr_{2-x}La_xCuO_y, allowing for the calculation of copper valence and oxygen content. The results from the DO/Cl method with DE correction show that the measured copper valence and oxygen content differ very little from those obtained using the iodometric titration method, with discrepancies within 0.016 and 0.008, respectively. Additionally, this method reduces the measurement time by one-third compared to the iodometric titration method. The results demonstrate that the DO/Cl method with DE correction can effectively measure the copper valence and oxygen content in cuprate superconductors, and using hydrochloric acid as the experimental solution is superior to sulfuric acid and nitric acid.

Keywords: oxygen content; Cu valence; DO sensor; chlorine sensor; Bi₂Sr_{2-x}La_xCuO_y; superconductor



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1. Introduction

It is widely recognized that the Cu valence can significantly influence the transition temperature (T_c) of copper oxide superconductors [1,2]. The Cu valence correlates with the carrier concentration, and the valence can be deduced from the oxygen content by adhering to the charge neutrality principle. Considering Bi₂Sr_{2-x}La_xCuO_y [3], with assumed valences of Bi³⁺, Sr²⁺, La³⁺, and O²⁻, the formula relating the oxygen content (y), La content (x), and copper valence (v) simplifies to $y = (10 + x + v)/2$.

Over recent decades, a variety of methods for measuring oxygen content have been introduced (Table 1). Physical methods to measure oxygen content include thermogravimetric analysis (TGA) [4,5], X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and oxygen analyzers. Among these, TGA is a traditional method for measuring the loss of oxide material mass during controlled heating. Thermogravimetric analyzers (TGAs) range in price from approximately JPY 4,843,800 to JPY 24,219,000. Nevertheless, this method falls short of ascertaining the absolute oxygen content. Moreover, XPS and AES can measure the oxygen content in samples that contain at least 1 µg, but these methods are sensitive to the surface [6]. X-ray photoelectron spectrometers (XPS) range from approximately JPY 48,438,000 to JPY 129,168,000, with high-end models exceeding JPY 161,460,000. Auger electron spectrometers (AES) range from approximately JPY 32,292,000 to JPY 113,022,000. Impurities like carbonate or hydroxide tend to form near the surface. To mitigate the impact of these impurities, the surface needs to be scraped under high

vacuum conditions. Oxygen analyzers are priced between approximately JPY 1,614,600 and JPY 8,073,000.

Chemical analysis offers a more precise measurement of oxygen content compared to physical methods, achieving an accuracy of approximately 0.1%. The iodometric titration method, for instance, is frequently employed to ascertain the oxygen content in single-phase $\text{HgBa}_2\text{CuO}_{4+\delta}$ [7]. Furthermore, the enhanced coulometry technique has demonstrated reproducibility within 0.01% for $\text{YBa}_2\text{Cu}_3\text{O}_y$ reference samples weighing 310 mg [2,8].

Table 1. Oxygen content measurement methods.

Type	Method	Weight	Error	Time	Merit	Demerit
Physical analysis	Thermogravimetric analysis (TGA) [9]	0.1 mg	0.1%	1 h	High accuracy	Cannot ascertain the precise oxygen content.
	X-ray Photoelectron Spectroscopy (XPS) [10]	1 μg	>10%	1 h	The depth profile can be determined.	Sensitive to the surface Lacks precision
	Auger Electron Spectroscopy (AES) [10]	1 μg	~10%	1 h	The depth profile can be determined.	Sensitive to the surface Lacks precision
	Oxygen Analyzer [11]	1 g	~10%	10 min	Simple measuring	Requires a large sample Limited accuracy
Chemical analysis	Coulometric [12]	50 mg	0.1%	1 h	Minor error Automatic measurement	Long measurement time
	Iodometric [13]	50 mg	0.1%	1 h	Simple measuring	Long measurement time

We previously reported a novel technique called the dissolved oxygen (DO) method, along with a correction procedure, to determine the oxygen content in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ using a DO sensor. This method was also successfully applied to measure the oxygen content in $\text{YBa}_2\text{Cu}_3\text{O}_y$, and succeeded in measuring the oxygen content simply in one-third of the time required by the iodometric titration method. When compared to the iodometric titration method, the corrected errors for the Cu valence (v) and oxygen content (y) were confined to 0.026 and 0.039, respectively.

In this study, we hypothesized that not only O_2 but also Cl_2 gas is generated when dissolving Bi-based superconductors, and developed a dissolved oxygen/chlorine (DO/Cl) method with differential equation (DE) correction. This method uses not only a dissolved oxygen sensor but also a dissolved chlorine sensor to measure the dissolved oxygen and dissolved chlorine content in $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$, allowing for the calculation of copper valence and oxygen content. Notably, the total cost of the sensors and USB transducer used in the DO/Cl method with DE correction in this study is only around JPY 200,000, making it cheaper compared to other physical analysis methods.

2. Experimental

2.1. Preparation

Figure 1 illustrates a flow chart outlining the preparation process and subsequent determination for $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$ with x values of 0, 0.2, 0.4, 0.6, and 1. Bi_2O_3 , SrCO_3 , La_2O_3 , and CuO were ground and mixed using a solid-state reaction method, then calcined at 700 °C for 12 h in air. After cooling in the furnace, the mixture was ground again, mixed, and pressed into pellets. These pellets were then sintered at 850 °C for 20 h to synthesize the desired $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$ compounds.

The phase purity of the samples was confirmed through X-ray diffraction (XRD) analysis, confirming the presence of a single phase. Samples that did not exhibit single-phase characteristics were subjected to an additional sintering cycle at 850 °C for 20 h.

To quantify the oxygen content, the iodometric titration method was employed as the standard. The obtained values were then compared with those determined through the methods of DO/Cl and DO/Cl with DE correction.

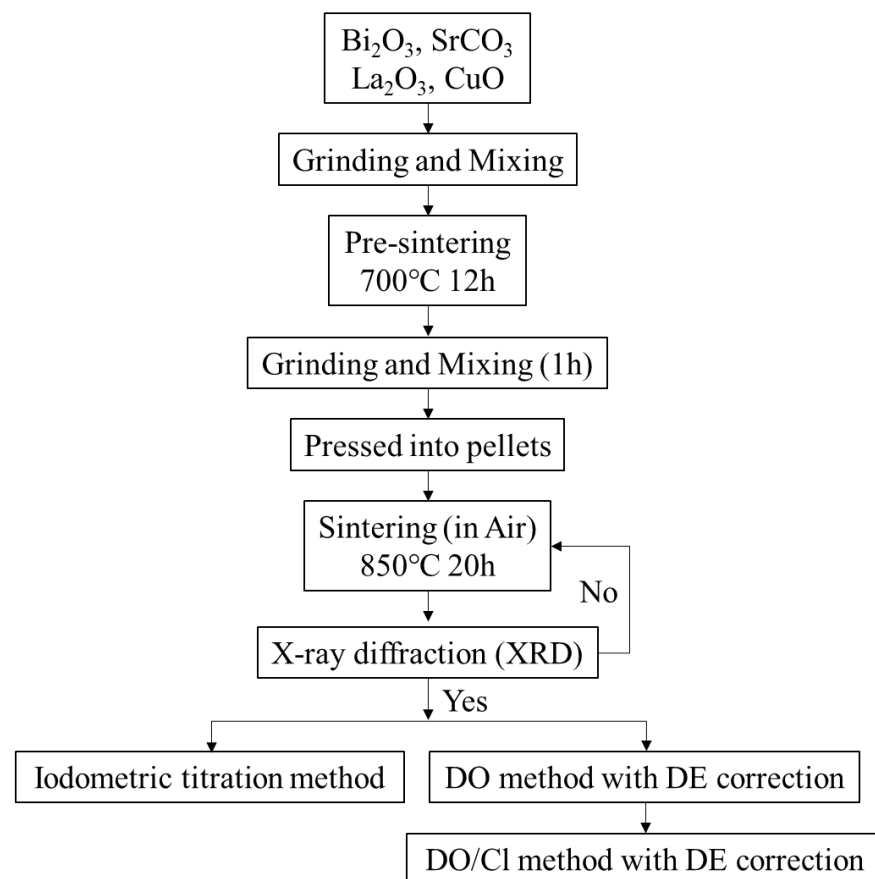


Figure 1. Experimental flow chart.

2.2. XRD

To verify the $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$ phase at room temperature, X-ray diffraction (XRD) analysis was conducted using a RIGAKU Ultima IV diffractometer (Rigaku Corporation, Tokyo, Japan) with $\text{Cu K}\alpha$ radiation. The instrument was set to a voltage of 40 kV and a current of 20 mA. Measurements were taken over a 2θ range of 3 to 60° with a scanning speed of $5^\circ/\text{min}$. Detailed X-ray diffraction conditions for the X-ray diffraction analysis are provided in Table 2.

Table 2. XRD parameters.

Target	Cu
Voltage	40 kV
Current	20 mA
Scan axis	$2\theta/\theta$
Sampling angle	0.02°
Scan speed	$5^\circ/\text{min}$
Scanning range	$3^\circ\sim 60^\circ$
Cumulative number	1 time
Divergence slit width	$1/2^\circ$
Scattering slit width	8.0 mm
Receiving slit width	Open

2.3. Iodometric Titration Method

The iodometric titration method can be categorized into multiple titrations or a single titration [7]. In our experiment, we utilized a single titration method. Figure 2 depicts the experimental setup and procedure.

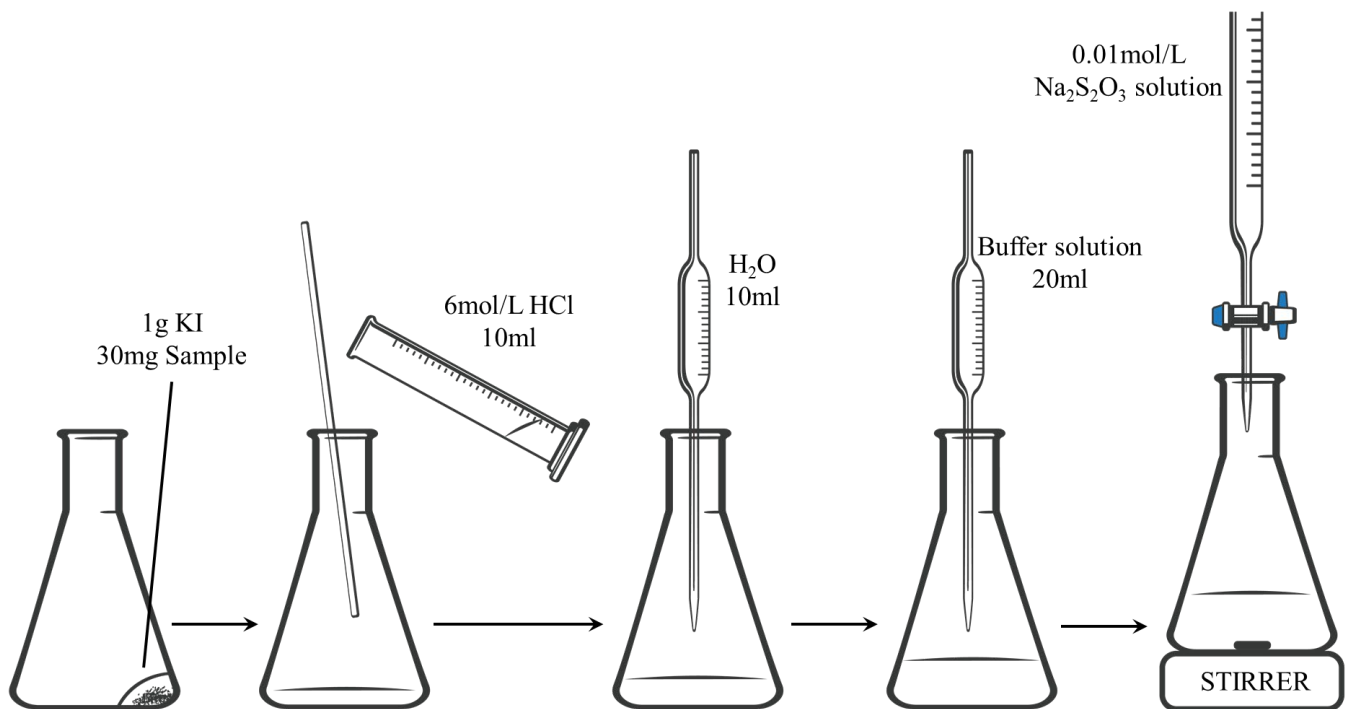


Figure 2. Experimental setup and procedure diagram for the iodometric titration method.

$\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$ powder (30 mg) was placed at the bottom of a beaker and then covered with 1 g of KI powder. Subsequently, 10 mL of 6 mol/L HCl was added to the beaker containing the mixture. The mixture was stirred with a glass rod for 10 min under an Ar gas flow to dissolve the powder. Next, 10 mL of distilled water was added, followed by 20 mL of a buffer solution (diluted acetic acid solution, used to adjust the pH to approximately 3). Then, 1 mL of starch solution was added as an indicator, turning the solution purple. Finally, a 0.01 mol/L of $\text{Na}_2\text{S}_2\text{O}_3$ solution was titrated until the color disappeared.

2.4. Dissolved Oxygen Method

The dissolved oxygen (DO) method was performed as described in the literature [14]. Initially, Ar gas was passed through 100 mL of 1 mol/L aq. HCl solution at a flow rate of 0.5 L/min while stirring to remove any dissolved oxygen. This degassing process, facilitated by argon bubbling, effectively reduced the background DO levels in the solution. After 10 min of treatment, the DO concentration stabilized within a range of 0 to 1 mg/L. Subsequently, 50 mg of $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$ was introduced into the solution. The resultant change in DO concentration was monitored and recorded. This entire measurement process was completed within 15 min.

Figure 3 illustrates the schematic diagram of the DO method. The DO sensor, interfaced with a PC through a USB transducer (DKK-TOA Corporation, Yamagata, Japan), is capable of gauging the DO concentration across a span of 0–19.99 mg/L. The transducer's dimensions are approximately 20 mm × 20 mm × 180 mm. It relays DO data to the connected PC in real-time, at one-second intervals, ensuring that the information is both displayed for immediate observation and archived for future reference. Moreover, the system is designed to automatically adjust the DO readings to account for variations in temperature, chloride ion concentration, and atmospheric pressure.

The fundamental principles governing dissolved oxygen measurement are extensively discussed in the literature [14]. When dissolving a metal oxide in an HCl solution, the metal's valence stabilizes to a fixed value. Specifically, if the initial valence of Cu is monovalent or trivalent, it converts to the divalent state upon dissolution. If the initial valence is higher than two, it also changes to the divalent state during dissolution, as follows:

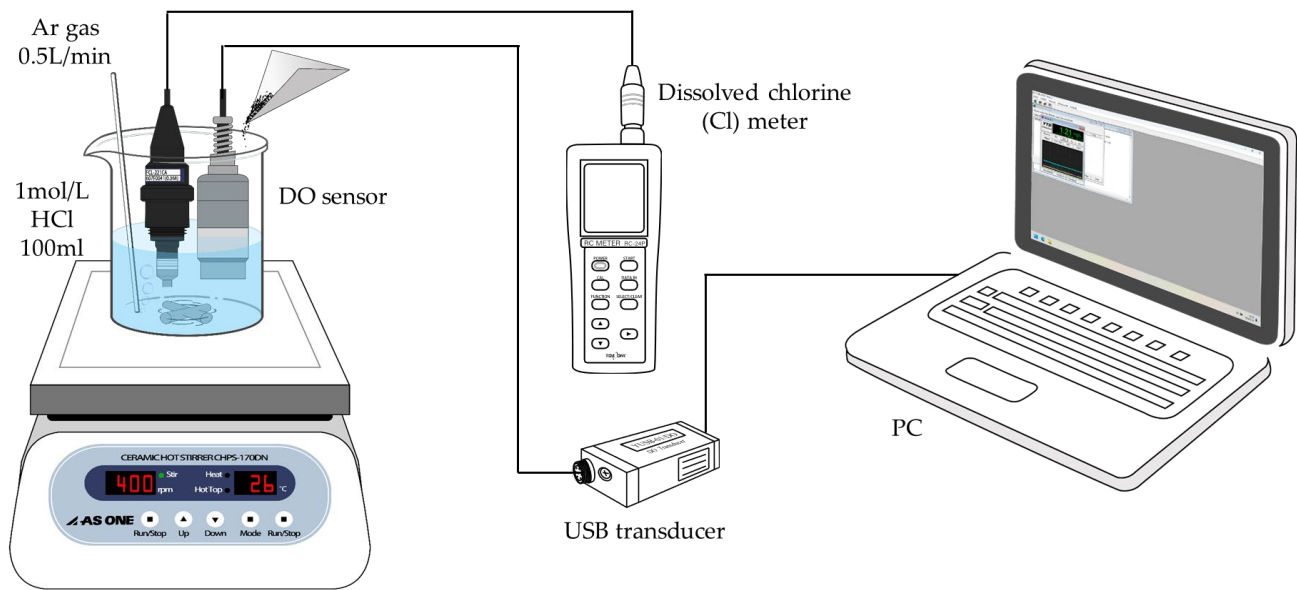
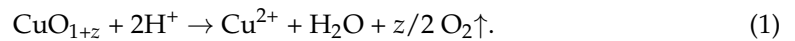
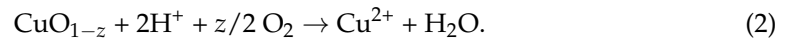


Figure 3. The schematic view of DO/Cl method with DE correction.



For Cu with a valence of less than two, it undergoes the following changes:



Since Equation (1) expresses the correlation between Cu valence and the DO content, the oxygen content of the oxide can be computed in the following manner.

$$\begin{aligned} m_{(\text{CuO}_{1+z})} &= w_{(\text{CuO}_{1+z})} / M_{(\text{CuO}_{1+z})} \\ m_{\text{O}_2} &= \Delta c \, V / M_{\text{O}_2} \\ 1:z/2 &= m_{(\text{CuO}_{1+z})} : m_{\text{O}_2} = \\ &= w_{(\text{CuO}_{1+z})} / M_{(\text{CuO}_{1+z})} : \Delta c \, V / M_{\text{O}_2} \\ \Delta c \, V / M_{\text{O}_2} &= (z/2) \times w_{(\text{CuO}_{1+z})} / M_{(\text{CuO}_{1+z})} \end{aligned}$$

We can obtain the equation to determine z :

$$z = 2 \times \Delta c \, V / M_{\text{O}_2} \times M_{(\text{CuO}_{1+z})} / w_{(\text{CuO}_{1+z})},$$

where $m_{(\text{CuO}_{1+z})}$, $w_{(\text{CuO}_{1+z})}$, $M_{(\text{CuO}_{1+z})}$, m_{O_2} , Δc , V , and M_{O_2} are molar number of CuO_{1+z} , weight of CuO_{1+z} (g), formula weight of CuO_{1+z} , molar number of O_2 , DO change (mg/L), volume of the solution (L), and formula weight of O_2 , respectively. In the case of the $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$ superconductor, $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$, CuO_{1+z} is substituted for CuO_{1+z} .

2.5. DO Method with Differential Equation Correction

When dissolving a sample, it not only dissolves oxygen but also partially degasses from the solution. Therefore, the change in dissolved oxygen (DO) does not fully represent all the dissolved oxygen. Here, a correction method is suggested [14]. If we assume that the rate of dissolution at time t_1 and the rate of degassing into the air both depend proportionally on the DO content, their relationship can be formulated as

$$d\Delta C / dt = -\alpha \Delta C \quad (3)$$

Rewriting with dt and ΔC on opposite sides:

$$d\Delta C / \Delta C = -\alpha \, dt$$

By integrating both sides of the equation:

$$\int d\Delta C / \Delta C = - \int \alpha dt$$

Integrating the left-hand side, we get:

$$\ln |\Delta C| = -\alpha t + C_1,$$

where C_1 is the constant of integration. Next, we express the result in exponential form:

$$|\Delta C| = e^{-\alpha t} + C_2$$

Since $|\Delta C|$ is greater than zero, we can remove the absolute value symbol and combine C_2 into a single constant C_1 , resulting in:

$$\Delta C = e^{-\alpha t} + C_1$$

If we denote ΔC at $t = 0$ as ΔC_0 ,

$$\Delta C = \Delta C_0 e^{-\alpha t} \quad (4)$$

where ΔC and ΔC_0 denote the dissolved oxygen (DO) amount at time t and at $t = 0$, respectively. This illustrates that after dissolution, the DO content exhibits an exponential decrease.

Taking the natural logarithm of ΔC

$$\begin{aligned} \log_{10} \Delta C &= \log_{10} \{ \Delta C_0 \exp(-\alpha t) \} \\ &= \log_{10} \Delta C_0 + \log_{10} \{ \exp(-\alpha t) \} \\ &= \log_{10} \Delta C_0 + \ln \{ \exp(-\alpha t) \} / \ln 10 \\ &= \log_{10} \Delta C_0 - \alpha t / 2.303 \end{aligned} \quad (5)$$

Figure 4a,b depict ΔC and the natural logarithm of ΔC as functions of time during the dissolution of a cuprate superconductor sample, respectively.

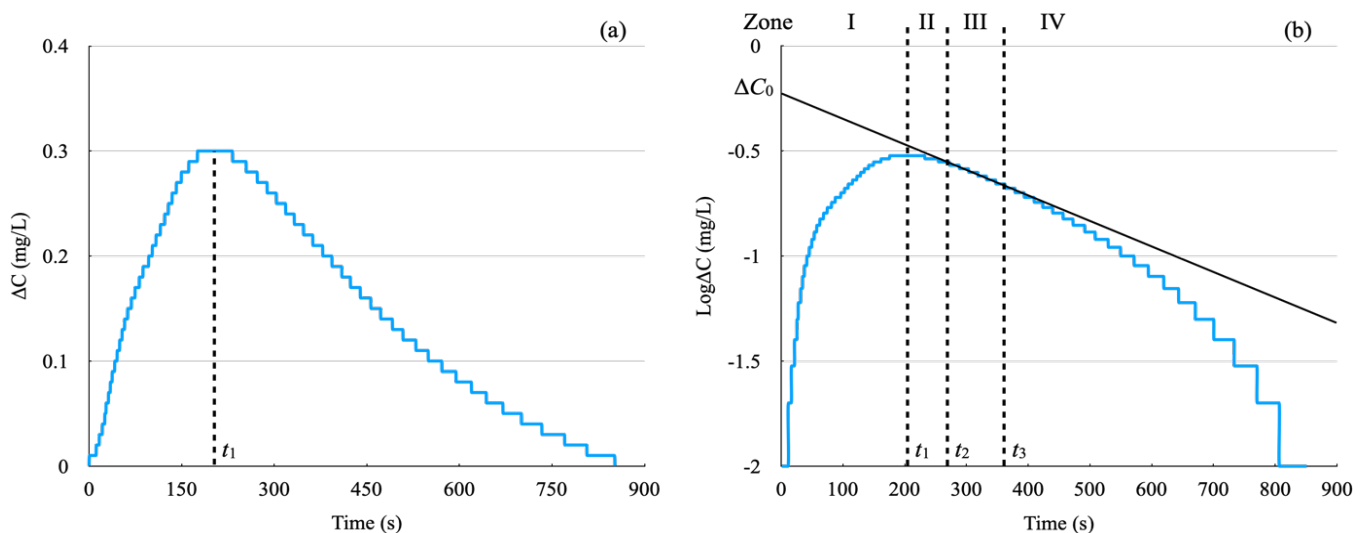


Figure 4. (a) shows the dissolved oxygen concentration, ΔC , plotted against time, while (b) depicts the natural logarithm of ΔC as a function of time.

As depicted in Figure 4a, for $0 \leq t < t_1$, the dissolved oxygen (DO) content increases as the sample continues to dissolve. Beyond t_1 , the dissolution rate slows down, leading to

a decrease in the DO content. For times beyond t_1 the data in Figure 4a,b should be fitted to Equations (4) and (5), respectively.

As noted in Equation (5), taking the logarithm of the DO content results in a linear relationship. Therefore, additional analysis will focus on Figure 4b.

In Figure 4b, the graph is segmented into four zones: Zone I ($0 \leq t < t_1$), Zone II ($t_1 \leq t < t_2$), Zone III ($t_2 \leq t < t_3$), and Zone IV ($t_3 \leq t$),

In Zone I, the dissolution of the sample leads to an increase in oxygen concentration.

In Zone II, the rate of oxygen release surpasses the rate of oxygen generation, resulting in a decrease in oxygen concentration in the solution. This phase is influenced by both the generation of oxygen through sample dissolution and the release of oxygen from the solution.

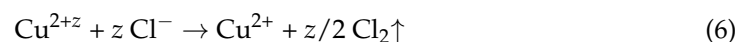
Zone III is characterized by the cessation of oxygen generation from sample dissolution, with oxygen release from the solution becoming predominant. Equation (5) applies in Zone III, resulting in a linear graph. Here, t_2 denotes the time when sample dissolution concludes, coinciding with the complete dissolution of the sample. For the $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$ sample, t_2 falls between 200 and 350 s. We determined t_2 and t_3 using the least squares method. When t_2 and t_3 lie on a straight line, the correlation function of the least squares method reaches its minimum value and remains constant. t_2 and t_3 were decided within the range where the correlation function is minimized and constant.

In Zone IV, the variation in oxygen concentration becomes smaller than the detection limit, causing the graph to deviate from a linear trend. This zone occurs when the dissolved oxygen level is within the range of $\log_{10}\Delta C \leq -0.9 \sim -1.5$. This value aligns closely with the measurement error of the dissolved oxygen sensor, which may vary slightly depending on specific conditions. After the sample dissolution is complete at t_2 , we can extrapolate the straight line from Zone III back to $t = 0$ using Equation (5) to determine ΔC_0 . This approach is known as the DO method with DE correction.

The amount of oxygen in the solution is represented by a sequential reaction model of oxygen generation and release. However, after the dissolution ends (from t_2 to t_3), since no oxygen is generated, it can be approximated only by the dissolved oxygen release Equation (4). The presence of a range (from t_2 to t_3) showing an exponential decrease indicates that the above approximation is valid.

2.6. DO/Cl Method with DE Correction

It is acknowledged that during the dissolution of certain oxides in hydrochloric acid, not only is oxygen released, but chlorine may also be liberated. This phenomenon can introduce potential errors in the DO method with DE correction. The reaction can be described by the following equation:



If Cl_2 gas is released during the dissolution of a superconductor, it will be detected by a dissolved chlorine sensor. The value of z obtained is then added to the Cu valence measured using the DO method with DE correction, resulting in the DO/Cl method with DE correction.

Two sensors, a dissolved chlorine sensor (RC-24P) (DKK-TOA Corporation, Yamagata, Japan) and the DO sensor, were placed into the solution. Once the dissolved oxygen and chlorine concentrations stabilized, approximately 50 mg of $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$ was added to the solution to observe changes in the concentrations of dissolved O_2 and Cl_2 . The Cu valence was then calculated using Equations (1) and (6).

2.7. Effect of Different Acidic Solutions in the DO/Cl Method with DE Correction

We investigated the application of different acidic solutions, including HCl , H_2SO_4 , and HNO_3 . Historically, HCl solution has been commonly used in the method. Here, we selected H_2SO_4 solution and HNO_3 solutions with the same concentration of 1 mol/L as the acidic media in our experiments to explore their effects on the experimental results.

3. Results and Discussion

3.1. XRD Analysis

Figure 5 presents the XRD patterns of $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$ ($0 \leq x \leq 1$). The observed peaks within this range confirm the absence of impurity phases. Notably, the XRD patterns agree with those expected for single-phase $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$, verifying the single-phase nature of the synthesized samples.

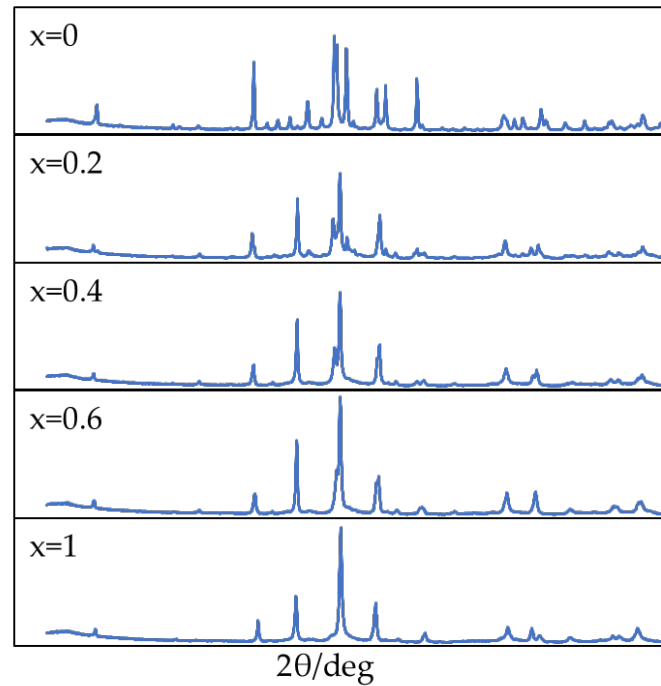


Figure 5. XRD patterns of $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$.

In Figures 6 and 7, we juxtaposed the XRD patterns for $x = 0$ and $x = 1$ against the corresponding single-phase JCPDS standards.

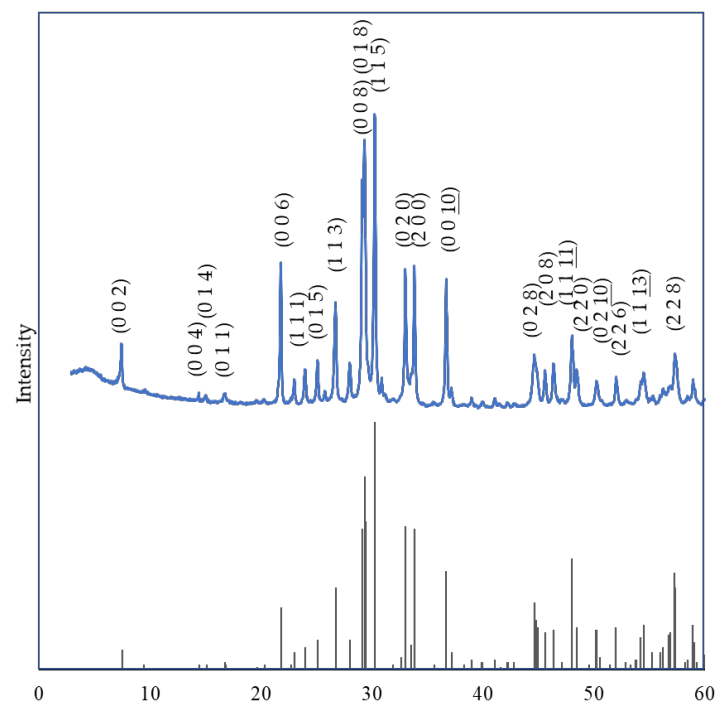


Figure 6. Comparison of XRD Patterns of $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$ ($x = 0$) with JCPDS.

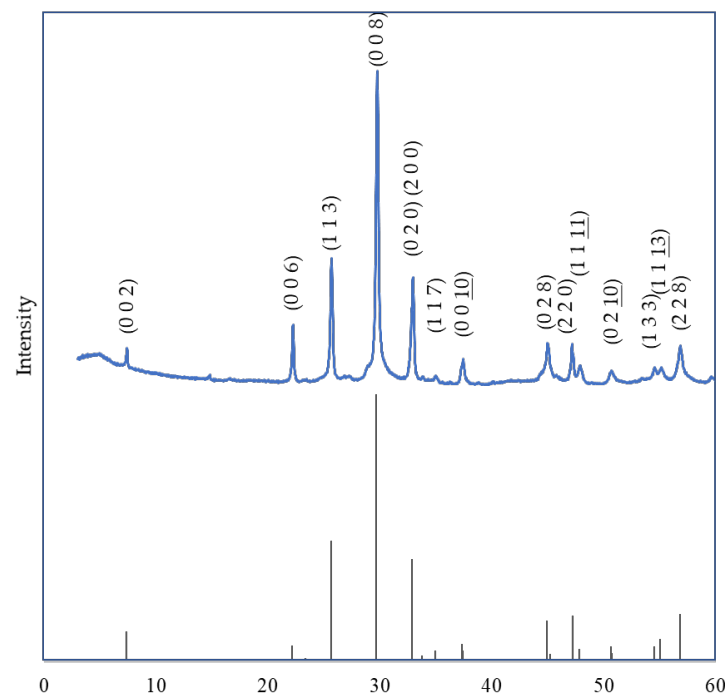


Figure 7. Comparison of XRD Patterns of $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$ ($x = 1$) with JCPDS.

3.2. Iodometric Titration Method Results as a Standard

Table 3 provides the Cu valence (v) and oxygen content (y) for $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$ across the range $0 \leq x \leq 1$. The values are deduced using the relation $y = (10 + x + v)/2$. The iodometric titration indicates a significant increase in oxygen content (y) with increased La doping levels. Enhanced La doping leads to the substitution of La^{3+} ions for Sr^{2+} ions. This modification could promote the integration of additional oxygen atoms.

Table 3. Cu valence (v) and oxygen content (y) of $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$.

La Content (x)	Iodometric	
	Cu Valance (v)	Oxygen Content (y)
x = 0	2.383	6.191
x = 0.2	2.459	6.330
x = 0.4	2.466	6.433
x = 0.6	2.460	6.530
x = 1	2.331	6.666

3.3. DO Method Analysis

Figure 8 illustrates the temporal variation of dissolved oxygen (DO) concentration, denoted as ΔC (mg/L), in hydrochloric acid. A consistent sample weight of 50 mg of $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$ is used throughout the experiments. The dissolution process employs 100 mL of 1 mol/L aqueous HCl solution. Upon the introduction of $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$ into the solution at time zero ($t = 0$), a notable increase in DO content is observed. The elevation in DO concentration is attributed to the oxygen release delineated in Equation (1). Over time, the dissolved oxygen gradually diffuses into the atmosphere, leading to a decrease in the solution's oxygen concentration.

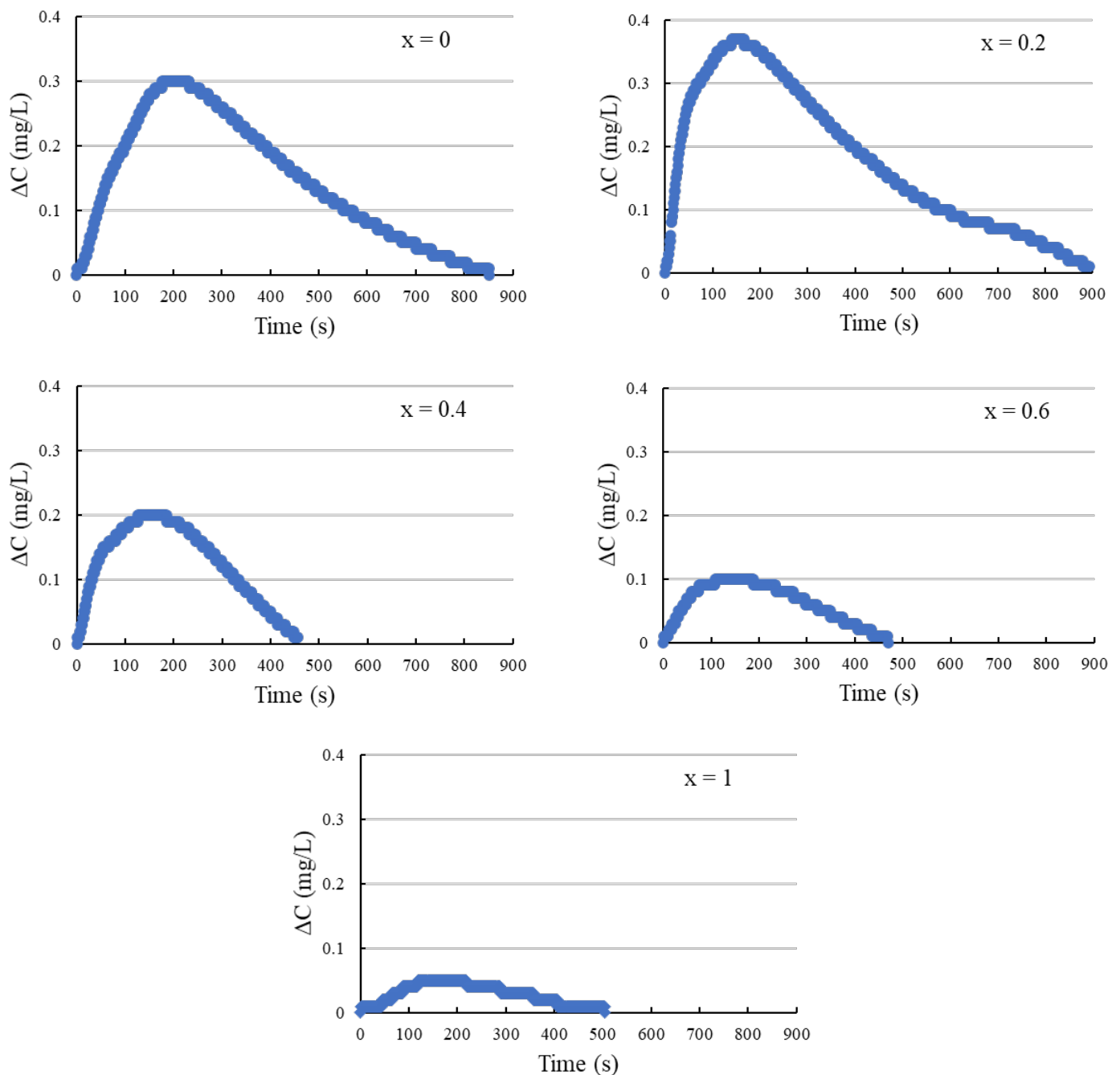


Figure 8. Change of DO concentration ΔC (mg/L) when $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$ is dissolved.

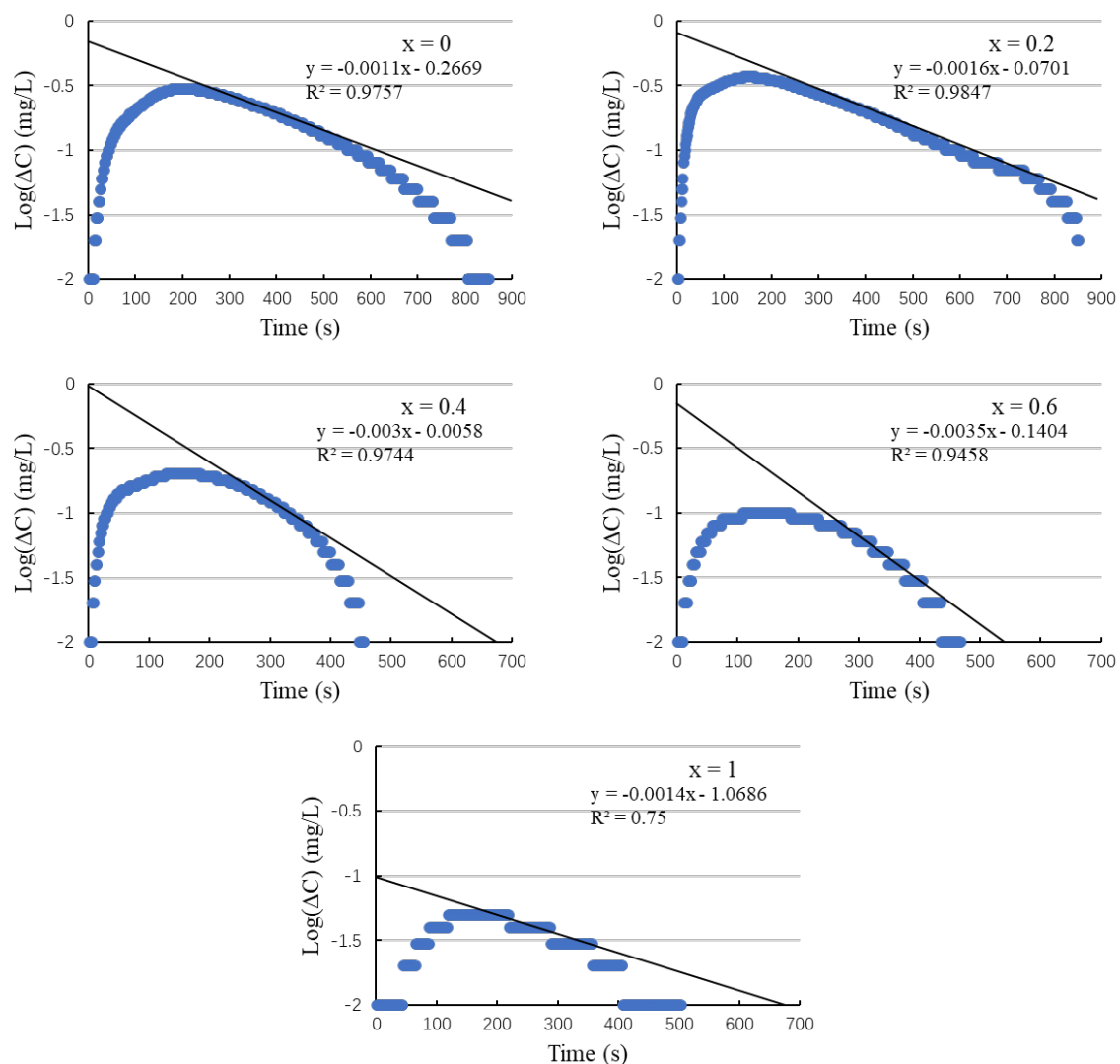
We quantify this change by measuring the difference (ΔC) between the peak DO value and the initial DO value at $t = 0$. Utilizing the DO concentration fluctuation and the solution's volume, we can deduce the copper valence (v) and oxygen content (y). Table 4 shows the Cu valence and oxygen content of $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$ measured using the DO method. The Cu valence (v) obtained by the DO method ranges from 2.005 to 2.071, while those obtained by the iodometric titration method range from 2.331 to 2.467, indicating that the values determined by the DO method are lower than those obtained through the iodometric titration method. This discrepancy suggests that the DO method yields lower valence values, likely due to oxygen release during the sample's dissolution phase.

Table 4. Cu valence (v) and oxygen content (y) of $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$.

La Content (x)	Iodometric		DO Method		DO Method with DE Correction		DO/CI Method with DE Correction	
	Cu Valance (v)	Oxygen Content (y)	Cu Valance (v)	Oxygen Content (y)	Cu Valance (v)	Oxygen Content (y)	Cu Valance (v)	Oxygen Content (y)
$x = 0$	2.383	6.191	2.056	6.028	2.101	6.050	2.387	6.193
$x = 0.2$	2.459	6.330	2.070	6.135	2.162	6.181	2.451	6.325
$x = 0.4$	2.466	6.433	2.038	6.219	2.190	6.295	2.469	6.434
$x = 0.6$	2.460	6.530	2.020	6.310	2.142	6.371	2.444	6.522
$x = 1$	2.331	6.666	2.010	6.505	2.017	6.509	2.329	6.665

3.4. DO Method with DE Correction

The oxygen contents measured by the DO method undergo refinement using a differential equation correction, as shown in Table 4. Figure 9 shows the relationship between the logarithm of the change in DO concentration ($\log \Delta C$) and time. After dissolution, ΔC exhibits an exponential decline, while $\log \Delta C$ decreases linearly. By extrapolating $\log \Delta C$ to $t = 0$, we infer the true initial value of ΔC , denoted as ΔC_0 in Figure 9. This extrapolation forms the basis of the DO method with DE correction.

**Figure 9.** Logarithmic ΔC as a function of time.

As outlined in Sections 2.2–2.5, the linear segment of the graph—indicative of a stable degassing rate—occurs once the $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$ sample is completely fully dissolved, specifically from $t = 200$ to 350 s, until $\log_{10}\Delta C$ reaches approximately -0.5 . For instance, the $x = 0$ sample achieves a logarithmically consistent degassing rate between 176 s (complete dissolution) and 232 s ($\log_{10}\Delta C = -0.5$). The coefficient of determination for the least squares analysis of this portion of the graph is greater than 0.9757 , indicating an excellent level of linearity. The data in Figure 9 allows for precise identification of the linear portion across various samples.

3.5. Comparison of DO Method with DE Correction and Iodometric Titration Method for Oxygen Content in $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$

We conducted a comparative analysis of the oxygen content in $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$ samples using two distinct methods: the DO method with DE correction and the traditional iodometric titration method.

In Table 4 and Figure 10a, we present a comparison of the oxygen content measurements obtained from both methods. The results indicate a consistent difference in the oxygen content values. The oxygen contents measured by the DO method with DE correction are approximately 0.138 to 0.160 lower than those obtained via the iodometric titration method.

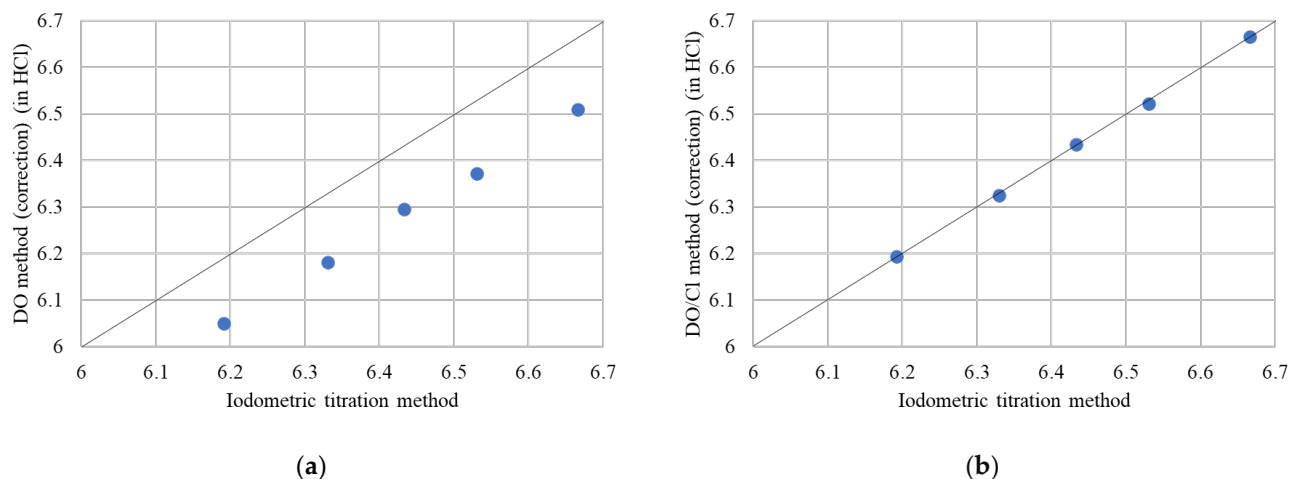


Figure 10. Oxygen content measured by (a) DO method with DE correction and (b) DO/Cl method with DE correction vs. the Iodometric titration method.

3.6. Comparison of DO/Cl Method with DE Correction and Iodometric Titration Method for Oxygen Content in $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$

The dissolution of a sample in an HCl solution often results in the formation of Cl_2 gas. Consequently, we observed an increase in dissolved chlorine, which was measured alongside the increase in dissolved oxygen (DO/Cl method with DE correction). The results are listed in Table 4. By incorporating the Cl method, the copper (Cu) valences aligned more closely with those obtained through iodometric titration.

Figure 10b illustrates a comparative analysis of the oxygen content determined by the DO/Cl method with DE correction against the iodometric titration method. The observed differences in oxygen content range from approximately 0.002 to 0.008 , underscoring the precision of the DO/Cl method with DE correction.

In summary, the utilization of the DO/Cl method with DE correction enhances the accuracy of the measurements. A comparative evaluation of the results from the DO/Cl method with DE correction against those from the uncorrected DO method with DE correction reveals a marked improvement, attesting to the efficacy of the technique.

In terms of measurement efficiency, the experimental duration required for the DO/Cl method with DE correction is significantly shorter—approximately one-third of the time

needed for the iodometric titration method. The DO/Cl method with DE correction not only demonstrates superior precision but also offers a reduced measurement timeframe, establishing itself as an efficient and reliable technique for determining the oxygen content in $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$.

3.7. Effect of Acidic Solutions on DO/Cl Method with DE Correction

In Table 5, Cu valence (v) and oxygen content (y) of $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$ by the DO/Cl method with DE correction in various acids are listed. In Figure 11, we present a comparative analysis of the oxygen content as measured by the DO/Cl method with DE correction in acids of HCl, H_2SO_4 , and HNO_3 against the iodometric titration method. The oxygen contents obtained via the DO/Cl method with DE correction in H_2SO_4 and HNO_3 were consistently lower than those measured by the iodometric titration method, with differences ranging from approximately 0.139 to 0.179 and 0.15 to 0.21, respectively. The discrepancies in oxygen content are attributed to the non-production of Cl_2 gas through Equation (6). It is to be noted that no Cl_2 gas is produced by dissolving in H_2SO_4 and HNO_3 acids.

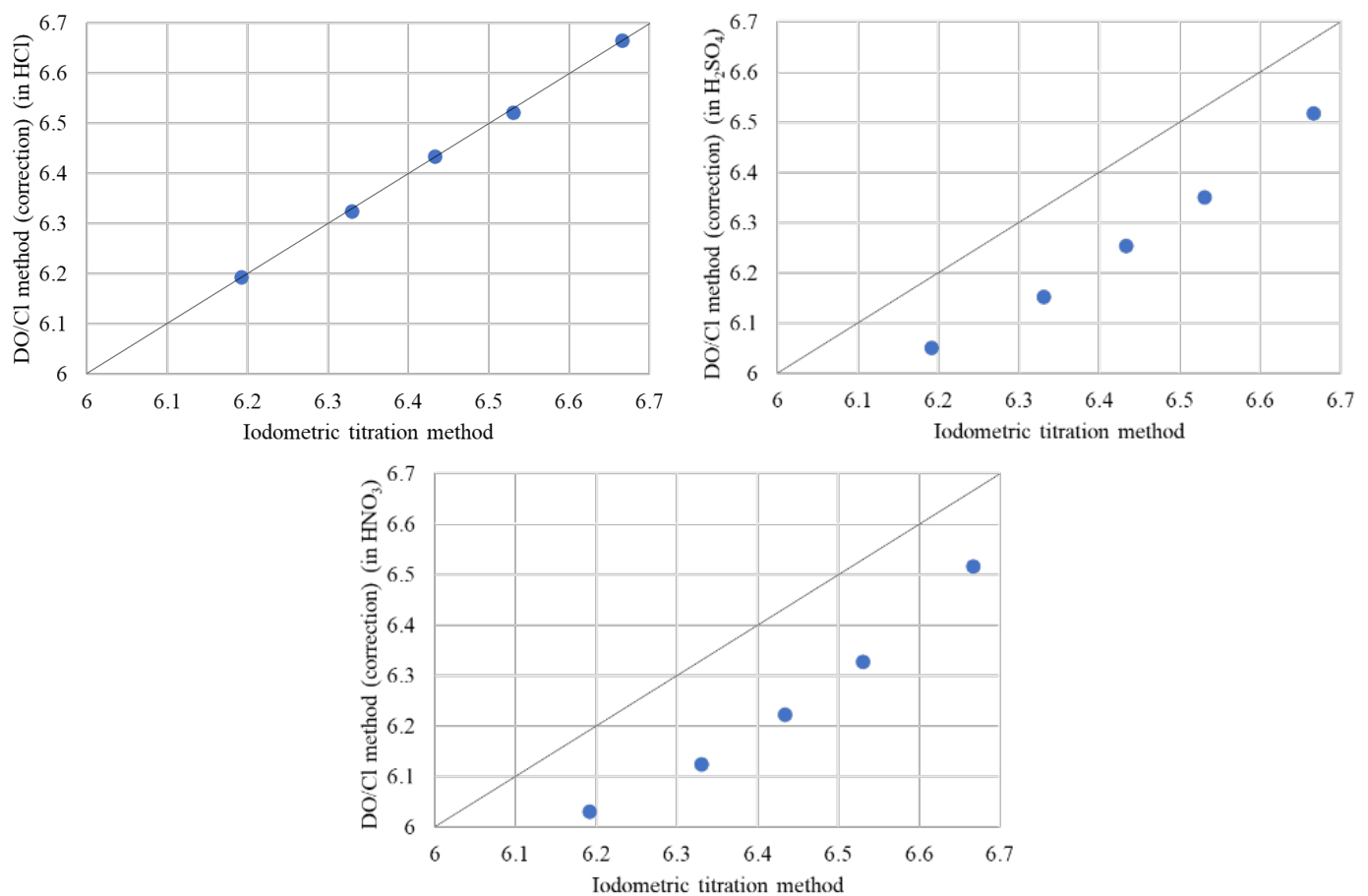


Figure 11. Oxygen content measured by the DO/Cl method with DE correction (in HCl, H_2SO_4 , HNO_3) vs. the Iodometric titration method.

Upon consideration of the experimental findings, it is evident that employing an HCl solution as the acidic medium in the DO/Cl method with DE correction enhances the accuracy of the experimental results.

Table 5. Cu valence (v) and oxygen content (y) of $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$ by DO/Cl method with DE correction in various acids.

La Content (x)	Iodometric		DO/Cl Method (in HCl)		DO/Cl Method (in H_2SO_4)		DO/Cl Method (in HNO_3)	
	Cu Valance (v)	Oxygen Content (y)	Cu Valance (v)	Oxygen Content (y)	Cu Valance (v)	Oxygen Content (y)	Cu Valance (v)	Oxygen Content (y)
$x = 0$	2.383	6.191	2.387	6.193	2.104	6.052	2.061	6.031
$x = 0.2$	2.459	6.330	2.451	6.325	2.106	6.153	2.051	6.125
$x = 0.4$	2.466	6.433	2.469	6.434	2.109	6.254	2.046	6.223
$x = 0.6$	2.460	6.530	2.444	6.522	2.102	6.351	2.056	6.328
$x = 1$	2.331	6.666	2.329	6.665	2.036	6.518	2.032	6.516

4. Conclusions

We hypothesized that not only O_2 but also Cl_2 gas is generated when dissolving Bi-based superconductors and developed a dissolved oxygen/chlorine (DO/Cl) method with DE. This method uses not only a dissolved oxygen sensor but also a dissolved chlorine sensor to measure the dissolved oxygen and dissolved chlorine content in $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$, allowing for the calculation of copper valence and oxygen content. The results from the DO/Cl method with DE correction show that the measured copper valence and oxygen content differ very little from those obtained using the iodometric titration method, with differences within 0.016 and 0.008, respectively.

Regarding measurement time, the experimental time of the DO/Cl method with DE correction is approximately one-third that of the iodometric titration method.

Compared to simply using the DO method with DE correction, the DO/Cl method with DE correction greatly improves accuracy.

In the selection of acidic solutions (HCl , H_2SO_4 , and HNO_3), using HCl solution for measurement yields the most accurate results. It is concluded that the DO/Cl method (in aq. HCl) with DE correction effectively determines the Cu valence and oxygen content of the superconductor $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$.

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