# Iodometric titration for determining the oxygen content of samples doped with Fe and Co

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## Abstract

Double iodometric titration is a method developed for high-$T_c$ superconductivity. It has been widely used to determine the effective oxidation of copper and to figure out the oxygen content in a sample in the past years. If a sample is doped with some metals like iron and cobalt, these metal ions can interfere in experiment results. This is a major defect for iodometric titration. To solve this problem, we introduce ammonium hydrogen fluoride as a complex agent into the method. The agent can prevent the interference of ions of iron and cobalt. For samples $LaBa_2Cu_{3-x}Fe_xO_y$ and $YBa_2Cu_{3-x}Co_xO_y$, we determine the oxygen content by an improved double iodometric titration in which the ammonium hydrogen fluoride is used as an interference-free agent. For samples doped with a small amount of Fe or Co, experiment results agree well with those of other researchers. As to samples doped with a large amount of Fe or Co, we determine their values of oxygen content and the results are reasonable.

## 1. Introduction

To reveal the source of superconductivity, an important method is to determine the effective oxidation level of copper in a sample. It is a necessary to study the effects of the copper substituting with metal ions, especially trivalent magnetic elements, like Fe or Co. Doping magnetic elements in a superconductor is a special step to approach some features we are interested in. First, it is believed that superconductivity and ferromagnetism are mutually exclusive. By doping a magnetic element we can observe the law of degradation of superconductivity with increasing content of magnetic ions. Second, Fe

doping makes it possible to observe the Mössbauer effect, which is a powerful method to study the physical and structural properties of a sample. For the above reason, Fe or Co is doped into the samples.

Thermogravimetric analysis (TGA) [1], the inert gas fusion nondispersive IR method [2], iodometric titration [3–6], and the like [7–9] are methods for determining the oxygen content of a superconductor. For TGA, if the oxygen content of the Fe doped sample increases, one cannot decide that it is either a result from appearing $Cu^{3+}$ or from increasing $Fe^{3+}$, with its number of valence higher than two. The inert gas fusion nondispersive IR method is seldom used because of the same problem. As to the iodometric titration, it can determine the effective copper oxidation level and then the oxygen content. It is a distinctive method that can avoid those defects. But

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$Fe^{3+}$ or $Co^{3+}$ in a sample can interfere in the iodometric titration. The following experiment results will show that with $Fe^{3+}$ or $Co^{3+}$ content small, the interference can make the experimental result deviate from the true one; with Fe content large, the interference is strengthened and sequently, a fleeting end point may be observed. Without modification, iodometric titration, therefore, is hardly used in measuring the oxygen content for a superconductor doped with Fe or Co. By means of adding a fluoride we put forward here an improved iodometric titration method to solve this problem.

## 2. Iodometric titration principle

The double iodometric titration, which is developed to reduce systematic errors [3], is generally used for high-$T_c$ superconductors. It consists of two titration experiments and their major reactions are stated as follows. In the first experiment, one dissolves a sample into an aqueous hydrochloric acid with excess KI, and a reaction occurs,

$$Cu^{2+p} + (2 + p)I^- = CuI\downarrow + 0.5(p + 1)I_2, \quad (1)$$
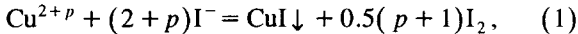
where $2 + p$ expresses the effective oxidation level of copper by the theorem of charge neutrality it sometimes is simply called the copper average valency. In the second experiment, by a special procedure, the number of valence of Cu in the sample is exactly equal to 2. Similar to reaction (1), we have

$$Cu^{2+} + 2I^- = CuI + 0.5I_2. \quad (2)$$
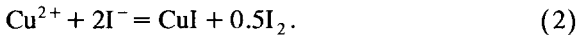
The liberated $I_2$ in Eqs. (1) and (2) are, respectively, titrated with a solution of sodium thiosulfate ($Na_2S_2O_3$). The reaction is

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6. \quad (3)$$
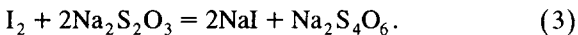
According to Eqs. (1) and (2), we do experiment 1 and 2, with the respective sample masses $m_1$ and $m_2$. The liberated iodine is titrated with a solution of $Na_2S_2O_3$ in the volumes of $V_1$ and $V_2$, respectively. If the average valency of Cu is expressed by $2 + p$, the $p$ may approximately be calculated by

$$p = (V_1/m_1)/(V_2/m_2) - 1. \quad (4)$$

## 3. The occurrence of interference

If iodometric titration is performed for a sample doped with $Fe^{3+}$, the $Fe^{3+}$ can react with I and release $I_2$ in the solution [10],

$$2Fe^{3+} + 2I^- = 2Fe^{2+} + I_2. \quad (5)$$
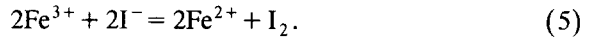
The $I_2$ released by $Fe^{3+}$ cannot be separated from that produced by copper. Thus, the $I_2$ appearing in the reaction (5) will also be titrated with the solution of $Na_2S_2O_3$. In this case, the used volume of the solution of $Na_2S_2O_3$ becomes larger, because $Fe^{3+}$ releases an added $I_2$. Obviously, the $Fe^{3+}$ causes an extra volume of the solution of $Na_2S_2O_3$, and there is an interferential error adding to the recorded data in this experiment. Since the discovery of high-$T_c$ superconductors, a lot of research works on the behavior of Fe or Co doped superconductors have been reported. However, we can hardly find anyone noting that $Fe^{3+}$ doped in a superconductor interferes in iodometric titration. Fortunately, difficulties by $Fe^{3+}$ are readily eliminated. Iron is rendered nonreactive by the addition of complex agents, such as fluoride; because these ions form more stable complexes with $Fe^{3+}$ rather than with $Fe^{2+}$, the potential for this system is altered to the point where appreciable oxidation of iodide cannot occur [11]. Ammonium hydrogen fluoride, $NH_4HF_2$, is a convenient buffer for this purpose. The anion of the salt dissociates as follows:

$$HF_2^- = HF + F^-, \quad (6)$$

$$HF = H^+ + F^-. \quad (7)$$

The first dissociation provides equal quantities of hydrogen fluoride and fluoride ions. The fluoride ions can make a complex with any present $Fe^{3+}$. Cobalt behaves similarly.

## 4. Experiments

### 4.1. Sample preparation

Samples were formulated by $RBa_2Cu_{3-x}M_xO_y$, where R = La and Y, M = Fe and Co, $x$ = 0, 0.03, 0.06, 0.1, 0.15, 0.25, 0.50, 0.75, 1.0, 1.5 and 2.0. The samples were prepared by high-temperature
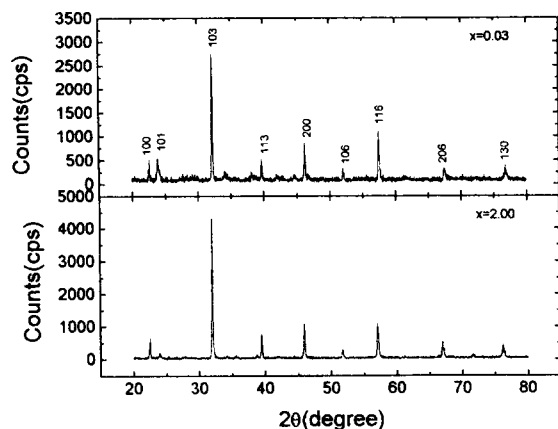
Fig. 1. X-ray diffraction patterns of $LaBa_2Cu_{3-x}Fe_xO_y$ with $x = 0.03$ and $2.00$.

solid-state reactions of CuO, $BaCO_3$, $La_2O_3$ and $Fe_2O_3$. The reactants were heated at 930°C for 24 h in air with furnace cooling. This was repeated. Then it was ground and pressed into flats. Again the samples were heated at 930°C for 24 h in flowing $O_2$, and cooled to 350°C at the rate of 1°C/min, kept at 350°C for 24 h, then cooled to room temperature by turning off the furnace.

The crystal structures of the final products (samples) were examined by powder X-ray diffraction analysis. X-ray diffraction patterns of Fe doped samples with $x = 0.03$ and $2.00$ are shown in Fig. 1. For samples with $x$ between 0.03 and 2.00, the diffraction patterns are similar. As to Co doped samples, results of X-ray diffraction were described in Ref. [12]. All structures of these samples doped with Fe and Co were characterized as orthorhombic or tetrag-

onal phases without obvious impurity phases appearing. For the samples, the effective oxidation level of copper and oxygen content were determined by an improved double iodometric titration as follows. For each sample, both experiment 1 and 2 were done three times to reduce experimental errors.

### 4.2. Experiment 1

About 50 mg $(m_1)$ of the sample weighed accurately was placed in a 100 ml Erlenmeyer flask, filled with flowing nitrogen gas. 10 ml of 3 N HCl dissolving 1 g of KI was added, utilizing a magnetic stirrer. After the sample is decomposed completely, we added 20 ml of a 1.5 N buffer solution, which consists of 3 N $NH_4Ac$ and 3 N HAc. The proper amount of buffer solution should be added so that the final pH of the solution is about 3.5. Then we added 8 ml of 20% ammonium hydrogen fluoride, $NH_4HF_2$. Next we titrated the solution with 0.01 N solution of $Na_2S_2O_3$ to approach the starch end point, then added 5 ml of 20% KSCN and continued to titrate to the KSCN end point. The total used volume of $Na_2S_2O_3$ solution is recorded as $V_1$ in ml.

### 4.3. Experiment 2

We placed about 50 mg $(m_2)$ of the sample weighed accurately in a flask, and dissolved it with 10 ml of 3N HCl. Next we heated the solution with the dissolved sample on a steam bat for 5 min, then let it cool to room temperature. We blanketed the flask with flowing $N_2$ and added 20 ml of 3 N buffer

Table 1

Values of the ratio $V/m$ vs. Fe content. The sign $+F$ represents the case with $NH_4HF_2$

| Fe content $x$ | $V_1/m_1$ (ml/mg) | $V_1/m_1$ (ml/mg) + F | $V_2/m_2$ (ml/mg) | $V_2/m_2$ (ml/mg) + F |
|---|---|---|---|---|
| 0.00 | 0.499 | 0.500 | 0.422 | 0.422 |
| 0.03 | 0.501 | 0.498 | 0.424 | 0.418 |
| 0.06 | 0.512 | 0.496 | 0.430 | 0.415 |
| 0.10 | 0.515 | 0.496 | 0.424 | 0.407 |
| 0.15 | 0.520 | 0.494 | 0.422 | 0.400 |
| 0.50 | 0.532 | 0.473 | 0.425 | 0.352 |
| 0.75 | 0.546 | 0.458 | 0.425 | 0.317 |
| 1.00 | | 0.437 | | 0.280 |
| 1.50 | | 0.402 | | 0.212 |
| 2.00 | | 0.392 | | 0.168 |

solution. Stirring was done with a magnetic stirrer and then we added 8 ml of 20% $NH_4HF_2$. As soon as we added 1 g of powdered KI, we titrated the solution with 0.01N ($V_2$ ml) $Na_2S_2O_3$ solution to the starch and KSCN end points.

## 5. Results and discussion

For samples doped with iron, we performed the double iodometric titration as usual, in which no interference-free agent is added. Experiment shows that the end point in the titration becomes turbid as the sample contains iron. Furthermore, in the $LaBa_2Cu_{3-x}Fe_xO_y$ samples with $x \geq 0.75$, a fleeting end point appears. In the product, a constant end point cannot appear, no matter how much solution of $Na_2S_2O_3$ is added in. That leads to no result at all. To avoid that, surely, it is necessary to add the $NH_4HF_2$, acting as an interference-free agent. As a comparison, we do both double iodometric titrations with and without $NH_4HF_2$ added, and their ratios of $V/m$ are tabulated in Table 1, respectively. The quantities of $V/m$ without $NH_4HF_2$ are greater than the ones with $NH_4HF_2$, because of the interference by $Fe^{3+}$. Values of oxygen content of $LaBa_2Cu_{3-x}Fe_xO_y$ are shown in Fig. 2. In this figure, solid circles represent the results obtained by a usual double iodometric titration method and solid squares by the method with $NH_4HF_2$ as the above proposal. Values of the oxygen content obtained by the usual method are smaller than those with $NH_4HF_2$. However, when the Fe content is less than 0.15, the
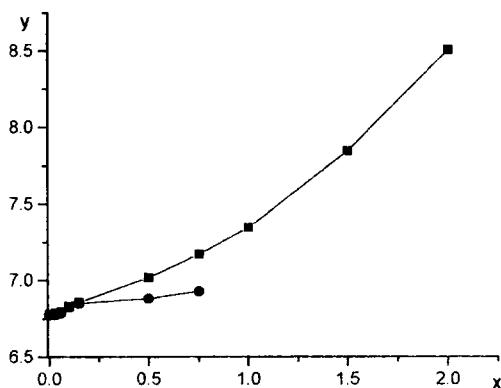


Fig. 2. For samples formulated by $LaBa_2Cu_{3-x}Fe_xO_y$, the oxygen content $y$ depends on the doped Fe content $x$.
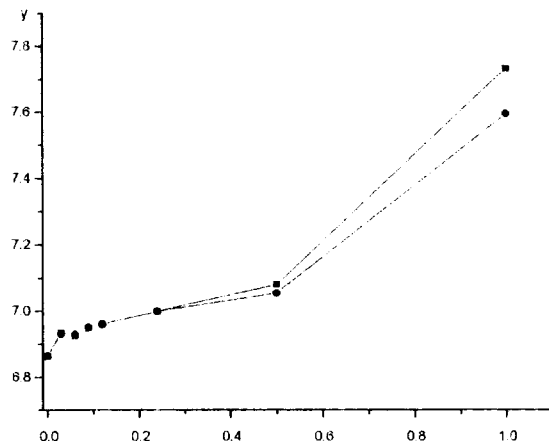


Fig. 3. For $YBa_2Cu_{3-x}Co_xO_y$ samples, the oxygen content $y$ changes with Co content $x$.

differences between the two methods with and without $NH_4HF_2$ are not significant, and the results conform to others [2]. When the Fe content increases, the differences between them become greater and greater. When $x > 0.75$, the method without $NH_4HF_2$ becomes useless; results can be only obtained with $NH_4HF_2$. This phenomenon had been observed in Ref. [13], that is, the oxygen content of samples doped with Fe could not be obtained when $x > 0.8$. It is noted that their oxygen content was determined by the usual iodometric titration method, and without any interference-free agent. However, that will cause the values of oxygen content to be lower, as shown in Fig. 2.

As to samples doped with cobalt, $Co^{3+}$ can interfere in the iodometric titration procedure as well. To see how different they are, we do both double iodometric titrations with and without $NH_4HF_2$ added. For $YBa_2Cu_{3-x}Co_xO_y$, the interference of Co, like iron, makes values of the ratio $V/m$ increase and the oxygen content decrease. The values of the ratio $V/m$ of samples doped by Co are similar to that doped by Fe, and have not been tabulated. The oxygen contents are shown in Fig. 3. In Fig. 3, solid circles and squares represent the values obtained by the usual double iodometric titration method without $NH_4HF_2$ and by the improved one with $NH_4HF_2$, respectively. For the usual method, with Co increasing the deviation of the values of the oxygen content becomes larger. Unlike Fe doping, there is not a fleeting end point to be observed even if the amount

of doped Co reaches as high as $x = 1$. It seems that the interference of Co is not as strong as that of Fe. As $x < 0.5$, the interference of Co is not large enough and the differences between the two methods with and without $NH_4HF_2$ can be omitted. In this case, our results agree with other researchers' results [14]. However, as $x > 0.5$, the interference becomes larger, the deviation of the oxygen contents is obvious. Recently, a series of $LaBa_2Cu_{3-x}Co_xO_y$ samples with $x$ from 0 to 1.0 has been reported [12], in which the oxygen contents were determined by the usual iodometric titration method without any interference-free agent. According to the preceding discussion, we suppose that their values of oxygen content should be lower than those with the interference-free agent.

For samples doped with a large amount of Co or Fe, such as $x \sim 1.0$, reports on the oxygen content have hardly been found yet, except Refs. [12] and [13]. In view of the preceding discussion, the results of the oxygen content we report here are more reasonable than those by iodometric titration without $NH_4HF_2$.

## Acknowledgements

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