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Spectrophotometric method for rapid estimation of the oxygen stoichiometry in YBCO superconducting samples

Research Article

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Abstract: Detailed investigations on the possibility for determination of the oxygen stoichiometry in $YBa_2Cu_3O_y$ superconducting samples by measuring the absorbance of the colored Co(III)-EDTA and Cu(II)-EDTA complexes in one solution have been performed. The absorptivity of the complexes at pH 2.5 and 4.9 as well as Beer's law have been studied. The content of the solution for the sample dissolving has been established. The stoichiometry of the oxidation-reduction reaction between Cu(III) from the sample and Co(II) in the solution has been proved. The possibility to dissolve the sample in air has been tested. As a result a simple and rapid spectrophotometric method for the determination of the δ non-stoichiometric oxygen coefficient in $YBa_2Cu_3O_{6.5+\delta}$ samples has been developed without precise measurement of the sample mass. The standard deviation of the δ- and y-coefficient results is 0.017. The reproducibility of the y-values in relative units (s_r) is 0.2%. The accuracy of the results has been confirmed by the method, which is based on the absorbance measurement of the I_3^- - starch compound.

Keywords: *Oxygen stoichiometry • YBCO superconductors • Co(III) and Cu(II) determination • Spectrophotometry*

1. Introduction

Various high-T_c superconductive copper oxides, such as $YBa_2Cu_3O_y$ (y=6.5+δ), have been extensively studied as functional material for applications. All superconducting oxides possess a strong tendency for oxygen non-stoichiometry. It is proved that the non-stoichiometry oxygen content (δ-coefficient) has an effect on the physical, structural and chemical properties of the oxides. Therefore it is crucially important to determine the exact oxygen content.

There are many "wet" methods (iodometric titrations [1-7], coulometric titrations [8-10], spectrophotometric analyzes [11-15]) for the determination of the oxygen stoichiometry in $YBa_2Cu_3O_{6.5+\delta}$ (YBCO) superconductors. In all of the methods the sample is dissolved either in acid or in weakly acid medium, in the presence of reducers such as iodide ions [1-7, 11-15], Co (II) [16], Fe(II) [17,18] and others.

In almost all methods the sample is dissolved under an inert atmosphere. Purging the solution with inert gas is a procedure that prolongs the time and complicates the performance of the analysis. The only method that does not require the sample dissolution in inert atmosphere is that using Co(II) as a reducer [16]. According to the method the sample is dissolved in air, in a medium of sodium acetate-acetic acid buffer (pH = 4.2 ÷ 4.7), Co(II) (from 0.02 to 0.05 mol L^{-1}) and EDTA (from 0.015 to 0.025 mol L^{-1}). A color complex of Co(III)-EDTA is formed, its absorbance is measured and the percentage content

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of Cu(III) is calculated. But the method possesses some shortcomings for example the sample is slowly dissolved (2-3 h) and precisely measuring the sample mass is necessary in order to calculate Cu(III) content. The secondary standard $K_9Cu(TeO_6)_2$ is used in order to calibrate the function $A = \varepsilon bC$.

In this work a new method for the determination of the non-stoichiometric oxygen content in YBCO bulk sample using Co(II) as a reducing agent is developed. The sample is dissolved in the presence of chloride ions, Co(II) and EDTA, without removing the air from the solution. The pH of the solution is 2.5. Co(III)-EDTA and Cu(II)-EDTA complexes are formed in a medium of sodium acetate-acetic acid buffer (pH = 4.9) and their absorbance was measured. The innovations of the method are: dissolving the sample in a weakly acidic solution for about 2 minutes; formation of Cu(II)-EDTA complex and measuring its absorbance; calculation of the δ non-stoichiometric oxygen coefficient as a ratio of the concentrations of Co(III)-EDTA and Cu(II)-EDTA complexes; using salts CoF_3 and $CuSO_4$ as standards for calibrating.

2. Experimental procedure

2.1. Solutions and apparatus

The following solutions were used: 0.1020 mol L^{-1} $CuSO_4$ and 0.02018 mol L^{-1} $CoCl_2$ prepared from $CuSO_4$•$5H_2O$ (p.a.) and $CoCl_2$•$5H_2O$ (p.a.), respectively; 0.01168 mol L^{-1} Co(III)-EDTA was prepared by dissolving CoF_3•$5H_2O$ (p.a.) in 0.05 mol L^{-1} EDTA; 0.05 mol L^{-1} HCl; 0.1 mol L^{-1} EDTA; 2 mol L^{-1} KCl; a solution of 1.0 mol L^{-1} KCl, 5×10^{-3} mol L^{-1} HCl and 2.5×10^{-3} mol L^{-1} $CoCl_2$; a sodium acetate-acetic acid buffer (C_{NaAc} = 0.4 mol L^{-1} ; pH = 4.9 ±0.1).

Absorbance values were measured by a single-beam Spekol 11 spectrophotometer (Carl Zeis, Jena) using cells with path length of 5 cm.

2.2. Procedure

2.2.1. Calibration of the function $A_M = k_M C_M$ (M = Cu(II), Co(III), Co(II))

Volumes from 0.1 to 0.5 mL of the $CuSO_4$ solution, 8 mL of the KCl solution, 1.5 mL of the HCl solution, 5 mL of the buffer solution and 4 mL of the EDTA solution were transferred to 25 mL volumetric flasks mL and the solutions were diluted up to the mark. The calibration solutions of the Co(II) were prepared in the same way using volumes from 3.0 to 5.0 mL of the $CoCl_2$ solution instead of the $CuSO_4$ solution. The calibration solutions of the Co(III) were prepared introducing from 0.5 to 3.5 mL of the stock Co(III)-EDTA solution, 1.5 mL of the HCl solution, 5 mL of the buffer solution in 25 mL measuring flasks of mL and diluting up to the mark. The absorbance of Cu(II)-EDTA complex was measured at wavelengths of 730 nm, and this of Co(II)-EDTA and Co(III)-EDTA complexes – at 533 nm. A blank solution was used as a reference.

2.2.2. Analysis of YBCO bulk samples

Volume of 10 mL from the solution of KCl, HCl and of $CoCl_2$ was added to a 50 mL beaker mL. The EDTA solution (1.5 mL) was then added, drop-wise to the solution at constant stirring. 2÷6 mg of a bulk sample, previously powdered and homogenized, was then added to the beaker with vigorous stirring. After the sample dissolution, 3 mL of the sodium acetate-acetic acid buffer was added, then 1.0 mL of the EDTA solution. The absorbance of the solution was measured at wavelengths of 533 and 730 nm, in cells with path length of 5 cm, against a reference solution containing the same quantities of KCl, $CoCl_2$, EDTA and a buffer as in the sample solution.

The δ-coefficient is calculated by the equation:

$$\delta = 0.75(C_{Co(III)}/C_{Cu(II)}) \tag{1}$$

The $C_{Cu(II)}$ and $C_{Co(III)}$ concentrations of the Cu(II)-EDTA and Co(III)-EDTA complexes are found by the equations:

$$C_{Cu(II)} = A_{730}/k_{730}^{Cu(II)} \tag{2}$$

and

$$C_{Co(III)} = A_{533} / (k_{533}^{Co(III)} - k_{533}^{Co(II)}) \tag{3}$$

A_{730} and A_{533} are the absorbance values measured at wavelengths of 730 and 533 nm; $k_{730}^{Cu(II)}$, $k_{533}^{Co(II)}$ and $k_{533}^{Co(III)}$ are the coefficients of the calibration functions: $A = k_{730}^{Cu(II)} C_{Cu(II)}$, $A = k_{533}^{Co(II)} C_{Co(II)}$ and $A = k_{533}^{Co(III)} C_{Co(III)}$, respectively.

3. Results and discussion

3.1. Complexes of Co(III) and Cu(II) with EDTA and calculation of its concentration

Co(III)-EDTA and Cu(II)-EDTA complexes are formed when the sample is dissolved. Their absorbance has been measured in a medium of sodium acetate-acetic acid buffer (pH = 4.9), at wavelengths of 533 and 730 nm. The absorbance of the complexes is maximal at the t wavelengths indicated in Fig. 1. At 533 nm the Co(II)-EDTA complex also absorbs (curve 1, Fig. 1).

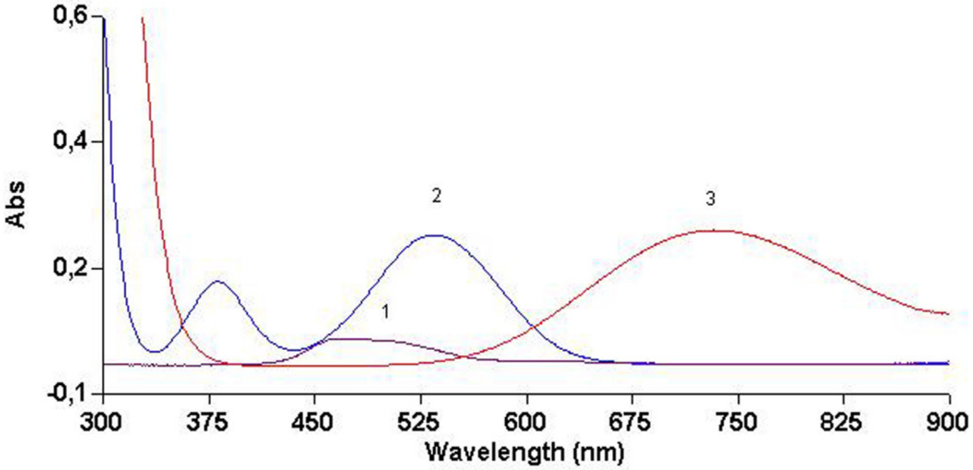

Figure 1. Absorption spectra of the complexes: (1) Co (II)-EDTA, (2) Co(III)-EDTA and (3) Cu(II)-EDTA in a sodium acetate-acetic acid buffer, b = 1 cm. $C_{Co(III)\text{-}EDTA} = 2.20\times10^{-3}$ mol L^{-1}; $C_{Cu(II)\text{-}EDTA} = 2.26\times10^{-3}$ mol L^{-1}; $C_{Co(II)\text{-}EDTA} = 5.00\times10^{-3}$ mol L^{-1}.

The absorptivity of the complexes is low and in order to increase the sensitivity of the determinations, cells with path length of 5 cm have been used.

The validity of Beer's law equation was tested and the coefficient values were calculated in a medium of sodium acetate-acetic acid buffer (pH = 4.9), as well as in the weakly acidic medium (pH 2.5), in which the sample has been dissolved (Table 1). It can be seen that the coefficient values of Co(III)-EDTA and Co(II)-EDTA complexes in the two media cannot be easily distinguished. The value of the coefficient of Cu(II)-EDTA complex in the solution with pH 4.9, however, is about two times higher than that found out in the solution with pH 2.5. A maximum absorptivity of Cu(II)-EDTA complex at pH value ≥5 is also cited in the literature [14] and hence in this work the absorbance of the complexes has been measured in solutions with pH 4.9.

The concentration of Cu(II)-EDTA complex has been calculated directly by Beer's law equation (Eq. 2). The equation for the concentration of Co(III)-EDTA complex (Eq. 3) is more complicated because the Co(II)-EDTA complex also absorbs at λ = 533 nm. In order to derive Eq. 3, Beer's law equation for additive absorbance has been used and the measurement of the sample solution against a reference solution of $CoCl_2$ has been taken into account. As the same quantity of $CoCl_2$ has been introduced both in the sample and in the reference solution, the equation for an additive absorbance is:

$$A_{533} = k_{533}^{Co(III)} C_{Co(III)} + k_{533}^{Co(II)} C_{Co(II)} - k_{533}^{Co(II)} C_{Co}^{total} \qquad (4)$$

where $k_{533}^{Co(II)} C_{Co}^{total}$ is the absorbance of the reference solution.

Substituting $C_{Co(II)} = C_{Co}^{total} - C_{Co(III)}$ in the above equation, Eq. 3 is obtained.

3.2. Conditions for sample dissolution

In order to find out the content of the solution for the sample dissolving, YBCO bulk sample was analyzed under an inert atmosphere. The apparatus used for the sample dissolving has been already described [12].

The investigations were carried out in the presence of chloride ions, EDTA and $CoCl_2$. A high quantity (10 mmol) of chloride ions introduced as KCl has been used for two reasons: 1) to increase the ionic strength of the solution aiming to dissolve the sample faster and 2) to stabilize the formation of $CuCl_i^{i-1}$ (i = 2, 3) complexes [19].

3.2.1. Effect of $CoCl_2$ and EDTA

Quantities of $CoCl_2$ and EDTA, 0.025 and 0.25 (0.15 + 0.10) mmol respectively, are enough for all complex forming reactions in the solution to be carried out quantitatively. In the presence of smaller quantities, outlying Cu(II) and Co(III) concentrations are observed at sample mass of above 6 mg (Fig. 2). Due to the slight solubility of EDTA in weakly acidic medium, its quantity has been introduced twice: before sample dissolving (0.15 mmol) and in the acetate medium (0.10 mmol).

3.2.2. Effect of HCl

Experiments conducted with and without HCl showed that the small quantity of HCl (0.05 mmol) introduced in the solution at sample dissolving stage do not exert any influence on the Co(III) and Cu(II) concentrations (Fig. 3). However this quantity is necessary in order to maintain the pH of the solution at about 2.5. In the weakly acidic medium the samples have been dissolved a little faster than in the neutral medium of KCl.

Table 1. Test of Beer's law.

Complex	pH	λ, nm	Concentration range, mmol L^{-1}	Number of determinations n	k ± Δk, P = 95%, f = n – 1 mol^{-1} L	Corr. coeff. r, %
Cu(II)-EDTA	2.5	730	0.80 ÷ 3.2	21	201 ± 5	99.6
Cu(II)-EDTA	4.9	730	0.22 ÷ 1.7	16	469 ± 4	99.9
Co(III)-EDTA	2.5	533	0.23 ÷ 1.9	24	554 ± 5	99.9
Co(III)-EDTA	4.9	533	0.23 ÷ 1.5	12	556 ± 7	99.9
Co(II)-EDTA	4.9	533	2.4 ÷ 7.3	12	41 ± 2	99.3

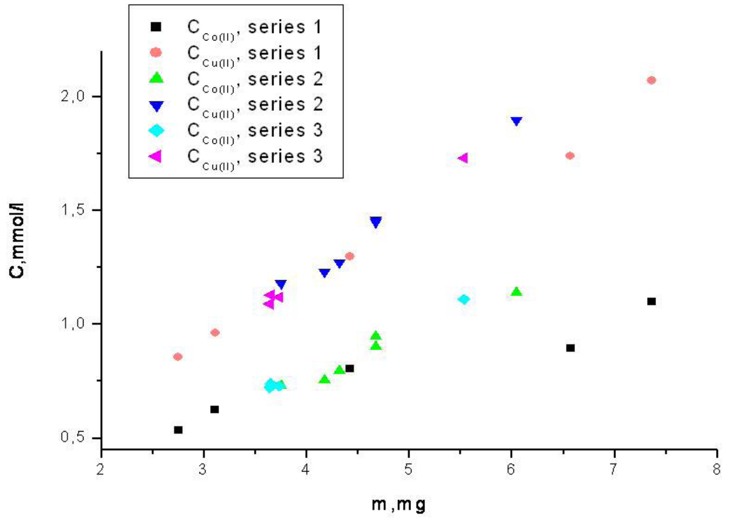

Figure 2. Influence of $CoCl_2$ and EDTA on Co(III)-EDTA and Cu(II)-EDTA concentrations in the presence of 10 mmol KCl and 0.05 mmol HCl. The quantities of $CoCl_2$ and EDTA are as follows: series 1 – 0.02 and 0.14 (0.06 + 0.08) mmol ; series 2 – 0.025 and 0.25 (0.1 + 0.15) mmol and series 3 – 0.04 and 0.25 (0.1 + 0.15) mmol.

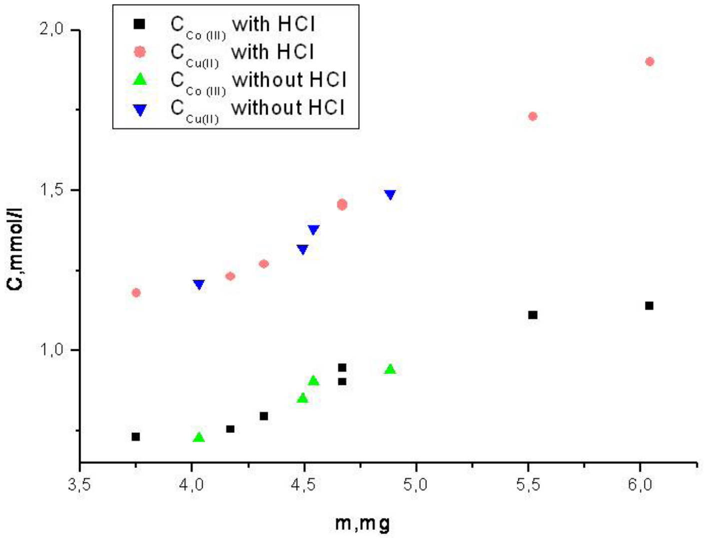

Figure 3. Influence of HCl on Co(III)-EDTA and Cu(II)-EDTA concentrations in the presence of 10 mmol KCl, 0.025 mmol Co(II) and 0.25 (0.15+0.10) mmol EDTA.

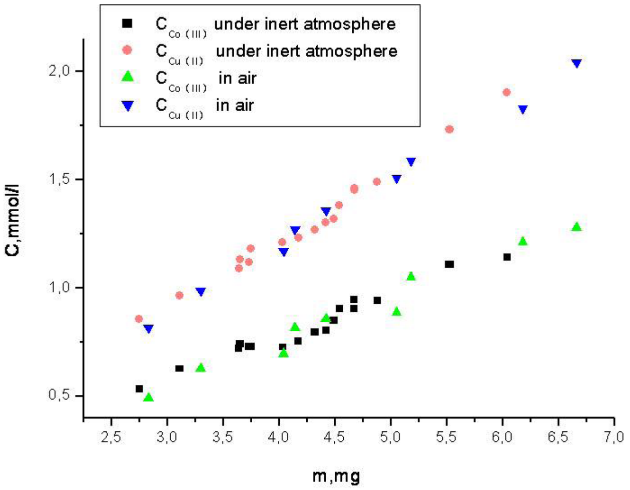

Figure 4. Co(III)-EDTA and Cu(II)-EDTA concentrations obtained by sample dissolving in air and under inert atmosphere.

3.2.3. Test for sample dissolving in air

The same YBCO bulk sample was analyzed following the procedure given in the experimental section. The points with coordinates Co(III) or Cu(II) concentration and a sample mass obtained by sample dissolving in air and under an inert atmosphere lie on the same straight line (Fig. 4).

3.2.4. Equation for the δ-coefficient

In order to derive the equation for δ-coefficient calculation, the stoichiometry of the reactions at sample dissolving has to be known. It supposes that in the presence of high chloride concentration the oxidation-reduction reaction between Cu(III) from the sample and Co(II) in the solution proceeds according to the following equation:

$$\begin{aligned} &Cu^{3+} + 2Co^{2+} + iCl^{-} + EDTA \rightarrow \\ &\qquad \rightarrow 2Co(III)\text{-}EDTA + CuCl_i^{i-1} \end{aligned} \tag{5}$$

The Cu(I) ions in the $CuCl_i^{i-1}$ complexes are oxidized by the air oxygen to Cu(II) and the latter form complex with EDTA.

Deriving from the above hypothesis, the ratio $\frac{n_{Cu(III)}}{n_{Co(III)}} = \frac{1}{2}$ is valid and the Cu (II) concentration calculated by Eq. 2 is equal to the total copper concentration: $C_{Cu(II)} = C_{Cu}^{total}$. By introducing the molar ratio and the Cu(II) and Co(III) concentrations instead of the molar quantities in the known δ-coefficient formulae

$$\delta = 1.5 \frac{n_{Cu(III)}}{n_{Cu(total)}}$$

[13,15], Eq. 1 is obtained.

In order to confirm the validity of Eq. 1, the δ-coefficient value was calculated from all the YBCO samples analyzed. The ratio $C_{Co(III)} / C_{Cu(II)} = 0.64 \pm 0.02$ (P = 95%; f = 26) was found out by regression analysis applied to the equation $C_{Co(III)} = k\ C_{Cu(II)}$ (r = 0.998) and was replaced in Eq. 1. The calculated δ-coefficient value was 0.48. The value of 0.49 was obtained from the analysis of the same YBCO bulk sample by the method based on the absorbance measurement of the I_3^--starch compound [15].

3.3. Precision and accuracy of the new method

The new procedure was applied to YBCO superconductors with different oxygen contents. Four $YBa_2Cu_3O_{6.5+\delta}$ monophase superconducting bulk samples, obtained as described in [20], and X-ray tested [20], were analyzed. The average values of the δ-coefficient and their confidence intervals (P = 95%, f = n-1) are shown in Table 2. The reproducibility of the δ-results of each YBCO bulk sample was estimated by standard deviation and is also shown in Table 2. The hypothesis $\sigma_1^2 = \ldots = \sigma_4^2 = \sigma_0^2$ was proved by applying Bartlet χ^2-criterium. As χ^2-value calculated (6.80) is lower than the χ^2-tabular value (7.81) with P = 95% and f = 3 [21], the standard deviation of the method is calculated by the formulae:

$$s = \sqrt{\frac{\sum_{j=1}^{m_i} \sum_{i=1}^{n_j} \left(y_{ij} - \bar{y}_j\right)^2}{n - m}} \quad [21]$$

where y_{ji} is the single result “i” in each sample “j”; $\bar{y}_j$ is the value of the mean result in the sample, m – number of the samples; n – total number of determinations.

Table 2. Results from YBCO bulk samples analysis, obtained by the new and comparative [15] methods.

YBCO	New method			Comparative method		
	Number of determinations n_j	Standard deviation s	Average value $\delta \pm \Delta\delta$	Number of determinations n_j	Standard deviation s	Average value $\delta \pm \Delta\delta$
YBCO-1	14	0.01848	0.486±0.011	5	0.00876	0.489±0.010
YBCO-2	5	0.00804	0.456±0.009	14	0.01544	0.448±0.009
YBCO-3	9	0.02092	0.382±0.016	12	0.02476	0.388±0.016
YBCO-4	3	0.00513	0.280±0.013	3	0.00403	0.272±0.010

Table 3. Test of the hypothesis $\sigma_{new} = \sigma_{comp} = \sigma_0$ and $\mu_{new} = \mu_{comp} = \mu_0$ of the results obtained by the new and comparative methods.

Hypothesis	$\sigma_{new} = \sigma_{comp} = \sigma_0$		$\mu_{new} = \mu_{comp} = \mu_0$	
Criteria	F_{calc}	F_{tabl}	t_{calc}	t_{tabl}
YBCO-1	4.45	5.91	0.34	2.11
YBCO-2	3.69	5.96	1.09	2.11
YBCO-3	1.40	3.34	0.59	2.09
YBCO-4	1.62	19.0	2.13	2.78

The standard deviation of the δ- and y- results is 0.017. Thus, the reproducibility of the method found out from 31 determinations of four YBCO bulk samples with different y-values (6.78 ÷ 6.99) in relative units (s_r) is 4% (for the δ-coefficient) and 0.2% (for the y-coefficient).

The spectrophotometric method, based on the absorbance measurement of the I_3^--starch compound was used as a comparison. The δ-values, as well as the estimation of their precision are also shown in Table 2. It is seen that the precision and the accuracy of the results obtained by the two methods do not differ considerably. The identity of the standard deviations $(\sigma^2_{new} = \sigma^2_{comp} = \sigma^2_0)$ and the absence of systematic errors $(\mu_{new} = \mu_{comp} = \mu_0)$ were confirmed statistically by applying Fisher's F- and Student's t-criteria [21]. The results are shown in Table 3.

4. Conclusions

Due to the formation of the colored Co(III)-EDTA and Cu(II)-EDTA complexes when $YBa_2Cu_3O_{6.5+\delta}$ samples are dissolved in the presence of Co(II) and EDTA, a spectrophotometric method for the determination of the δ-coefficient in the YBCO samples has been developed. The method does not require the sample to be dissolved under inert atmosphere or precise measurement of the sample mass; the analysis is performed easily and fast, and the results are precise and accurate.

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