

## Estimation of the oxygen content of $\text{RBa}_2\text{Cu}_3\text{O}_y$ ( $\text{R} = \text{Er, Y, Eu, Dy}$ ) superconducting samples by spectrophotometry and raman spectroscopy: a comparison between chemical and physical methods for oxygen determination

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**Abstract:** We have developed and applied a spectrophotometric method using measurement of the absorbance of the complex  $\text{Co(III)-EDTA}$  for the determination of the oxygen stoichiometry in  $\text{RBa}_2\text{Cu}_3\text{O}_y$  ( $\text{R} = \text{Er, Y, Eu}$  and  $\text{Dy}$ ) high- $T_c$  bulk materials. The obtained results were compared with those obtained by second destructive spectrophotometric method and Raman spectroscopy. The methods used show that the oxygen content of the  $\text{RBa}_2\text{Cu}_3\text{O}_{6.5+\delta}$  microcrystals is close to 7. The values of total oxygen content “ $y$ ” as well the non-stoichiometric coefficient “ $\delta$ ” were accurately calculated by the spectrophotometric method. The standard deviation of the  $\delta$ - and  $y$ -coefficient is 0.012. The reproducibility of the  $y$ -values is 0.2%. A comparison between chemical and physical methods for determination of the stoichiometry of REBCO thin films deposited on long-length metal substrates was done.

**Key words:** Superconducting materials; oxygen determination; spectrophotometry; cobalt; Raman spectroscopy.

### Introduction

Most of the high  $T_c$  superconducting oxides are cuprate compounds with a characteristic layered structure [1]. The cuprates  $\text{YBa}_2\text{Cu}_3\text{O}_y$  superconducting materials are characterized with non-stoichiometric oxygen content - “ $\delta$ ” ( $y = 6.5 + \delta$ ,  $\delta$  is the non-stoichiometric coefficient, active oxygen). The non-stoichiometric coefficient  $\delta$  acts as a regulating factor of the structural and electrical properties of the all cuprates RBCO ( $\text{R}$  is rare earth element) superconducting materials and its exact determination often meets serious difficulties. A lot of work has been done on the variation of stoichiometry and its effect on the superconducting properties of the material. However, in spite of all the work done, the results for oxygen determination of  $\text{RBa}_2\text{Cu}_3\text{O}_y$  superconductivity materials published in the literature are very scattered. The stoichiometry of these materials is the most important factor to consider in order optimizing its superconducting properties, and a great deal of work has been dedicated to the study of the variation in oxygen content of this material [1].

A number of destructive methods (“wet methods”) [2-17] have been used to evaluate the non-stoichiometric oxygen coefficient  $\delta$  in the  $\text{RBa}_2\text{Cu}_3\text{O}_y$  samples. Oxygen content could also be obtained by physical methods such as Raman spectroscopy and X-ray and neutron diffraction if appropriate mathematical relations “oxygen content - physical parameter” are preliminary known [18, 19]. Such mathematical relation between  $c$ -axis unit cell parameter (determined from Inorganic Crystal Structure database (ICSD) data) and the  $y$ -oxygen coefficient (determined by iodometric titrations) has been derived data for  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_y$  [19],  $\text{Er}_1\text{Ba}_2\text{Cu}_3\text{O}_y$ , and  $\text{Gd}_1\text{Ba}_2\text{Cu}_3\text{O}_y$  ceramics [16]. The new derived equations are used for the rapid semi-quantitative analysis of the oxygen content in the cited HTCS ceramics.

Raman spectroscopy registers the so-called Raman-active phonons. It serves to determine disorder, stoichiometry, superstructure, orientation, and impurity phases for the characterization of high- $T_c$  cuprates such as poly- and single-crystalline samples or epitaxial films. Its main objective is to

study the structure, the superconducting mechanism, and the metallic-to-insulating phase transition that occurs with a change of superconductivity. It is proved that one of the tools for *in situ* monitoring the direct deposition of YBCO films is Raman spectroscopy [1].

In this paper Raman spectra of YBCO coated conductor tapes for practical applications as well of REBCO (RE = Dy, Eu and Er) ceramics are presented. The determination of the oxygen content by both methods is discussed: a new simple and express spectrophotometric method based on measuring the absorbance of the solution of Cu(II)-EDTA and Co(II)-EDTA complexes and Raman spectroscopy. Moreover, a comparison between chemical and physical methods for stoichiometry determination of REBCO thin films deposited on long-length metal substrates was done. This will contribute for a rapid selection of method for monitoring of the oxygen content in superconducting materials deposited on substrates as well the superconducting wires depending of the purpose of analysis.

## Experimental

### Samples preparation

YBa<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub>, DyBa<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub>, EuBa<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> and ErBa<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> samples were prepared by standard solid state reaction. The appropriate amounts of high purity (all 99.99% pure) powders of Y<sub>2</sub>O<sub>3</sub>, Eu<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub>, Dy<sub>2</sub>O<sub>3</sub>, BaCO<sub>3</sub> and CuO were mixed, grounded, pressed into pellets and calcined in oxygen. This calcination was repeated three times. The first sintering was at 900°C in the flowing oxygen for 21 h. After grinding the powder was sintered at 930°C for the second time at the same atmosphere followed by slow cooling and additional annealing at 450°C for 2 h. The pellets were pressed at 5-6 MPa, sintered for the third time at 950°C for 23 h and subsequently annealed at 450°C for 23 h. The all sample are superconductive with the critical temperatures (T<sub>c</sub>) in the limits of T<sub>c</sub> = 90-93 K.

### Samples analysis by X-ray diffraction

Powder X-ray diffraction patterns were collected within the range from 5.3 to 80° 2θ with a constant step 0.02° 2θ on Bruker D8 Advance diffractometer with Cu Kα radiation and LynxEye detector. Phase identification was performed with the Diffracplus EVA using ICDD-PDF2 Database [20]. All of the samples are monophasic and their structure was determined to be orthorhombic one.

### Samples analysis by spectrophotometric method

The non-stoichiometric oxygen coefficient δ was determined by the spectrophotometric method based on the absorbance measuring of the colored Cu(II)-EDTA and Co(III)-EDTA complexes [17]. The sample was 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 is measured. The δ non-stoichiometric oxygen coefficient was calculated as a ratio of the concentrations of Co(III)-EDTA and Cu(II)-EDTA complexes by the equation

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

where C<sub>Cu(II)</sub> and C<sub>Co(III)</sub> are the concentrations of Cu(II)-EDTA and Co(III)-EDTA complexes obtaining by the equations:

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

and

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

A<sub>730</sub> and A<sub>533</sub> are the absorbance values measured at wavelengths of 730 and 533 nm; k<sub>730</sub><sup>Cu(II)</sup>, k<sub>533</sub><sup>Co(II)</sup> and k<sub>533</sub><sup>Co(III)</sup> are the coefficients of the calibration functions: A = k<sub>730</sub><sup>Cu(II)</sup> C<sub>Cu(II)</sub>, A = k<sub>533</sub><sup>Co(II)</sup> C<sub>Co(II)</sub> and A = k<sub>533</sub><sup>Co(III)</sup> C<sub>Co(III)</sub>, respectively.

The CoF<sub>3</sub> and CuSO<sub>4</sub> salts were used as standards for calibrating.

The method for oxygen content determination of superconducting materials deposited into substrates (thin films) was improved as in the sample dissolution solutions was introduced a piece of pure silver equivalent to that of the substrates (0.5 - 3 mg).

The absorbance of the solutions was measured by single-beam spectrophotometer Specol 11 (Carl Zeiss, Jena) with cells of 1 cm.

### Raman spectroscopy

The Raman spectra were measured using single Raman spectrometer LabRAM HR equipped with a microscope and Peltier-air-cooled CCD detector. The 633 nm line of a He-Ne laser was used for excitation. A 100X objective was used to both focus the incident laser beam onto a spot about 2 μm in diameter and to collect the scattered light in a backscattering geometry. The laser power on the spot was kept below 1 mW to prevent the possible local overheating. The polarization of the incident linearly polarized laser light was set using an achromatic half-wavelength plate. The scattered light was analyzed using a polarizer. The observations of polished surfaces of the ceramic samples show that the typical dimensions of the plate-like microcrystals, consisting of ceramics, are about several μm in direction perpendicular to the Cu-O

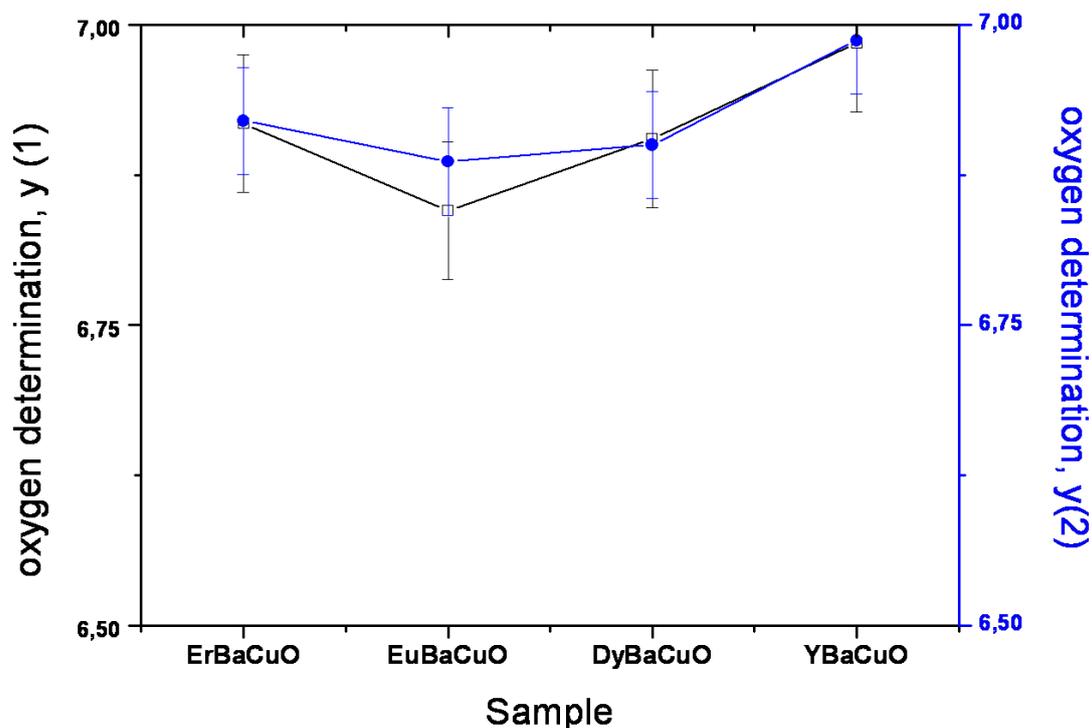
planes and 10 - 20  $\mu\text{m}$  in direction parallel to the Cu-O planes. No impurity phases were observed.

The microcrystals under investigation from the polished surface of the ceramics were chosen to be with regular rectangular shape. Additional criterion was their maximal change of the brightness and the color when the sample is rotated under linearly polarized white lamp illumination. Due to the strongly anisotropic electrical conductivity their color changes from brightly yellow (when the polarization of the light is parallel to the Cu-O planes) to darkly grey (when the polarization of the light is perpendicular to the Cu-O planes). Therefore, the orientation of the surface of the microcrystals chosen is of (mn0) type. From each spot investigated three types of Raman spectra [in Porto notations:  $y(zz)$ - $y$ ,  $y(xx)$ - $y$  and  $y(zx)$ - $y$ ] were obtained.

### Results and discussion

The non-stoichiometry coefficient ( $\delta$ ) in all  $\text{RBa}_2\text{Cu}_3\text{O}_{6.5+\delta}$  superconducting samples was

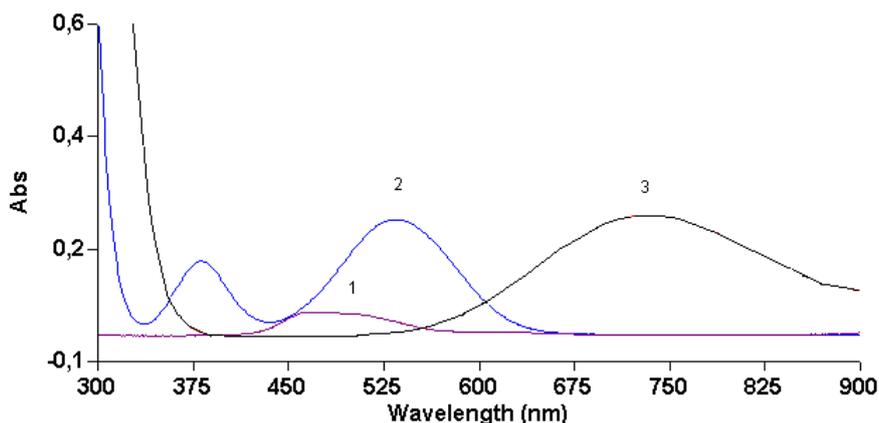
determined by the analytical method given in [17]. The method has been successfully applied for determination of oxygen content in YBCO superconductivity samples with different oxygen content [21] without precise measurement of the sample mass and its dissolving without removing the air oxygen. The sample mass used for analysis is about 1-2 mg which is a good solution for the analysis of the thin superconducting films. The values of the oxygen content “ $y$ ” are presented in Fig.1. The standard deviation of the  $\delta$ - and  $y$ -coefficient results is 0.012. The reproducibility (represented as standard deviation) of the  $y$ -values in relative units, (sr) is 0.2%. The accuracy of the results was confirmed by a comparative method, which is based on the absorbance measurement of the  $\text{I}_3^-$ -starch compound [14] (Fig. 1). One can see that the oxygen content of each sample is closed to 7. The different between the values of oxygen content determining by both methods are in the range of the random error (Fig. 1).



**Figure 1.** The values of the oxygen content  $y$  ( $y=6.5+\delta$ ) of  $\text{RBa}_2\text{Cu}_3\text{O}_{6.5+\delta}$  (RE= Er, Eu, Dy, Y) superconductors determined by two chemical methods ( $y(1)$ - the method using the absorbance measuring of the Cu(II)-EDTA and Co(III)-EDTA complexes [17];  $y(2)$  - comparative method given in [14])

The method would be applied for analyzing of the oxygen content in superconducting RBCO materials deposited on substrates (thin films). Usually the substrates for deposition of superconducting material contain 99,9 % pure silver [22]. The experiments for oxygen determination of bulk superconducting materials with model solutions containing silver were made. The sample has been dissolved in a weakly acidic medium (pH 2.5) according the procedure given in [17] in the presence

of piece of pure silver and the analytical signal has been measured in a medium of a sodium acetate-acetic acid buffer (pH = 4.9) at wavelengths of 533 and 730 nm [17]. At the pointed out wavelengths the Co(III) and Co(II)-EDTA ( $\lambda = 533$  nm) and Cu(II)-EDTA ( $\lambda = 730$  nm) complexes absorb only (Fig.2). One can see that the silver do not exert any effect on the absorption spectra of the three complexes and the obtained spectra of the complexes are the same of these given in [17].

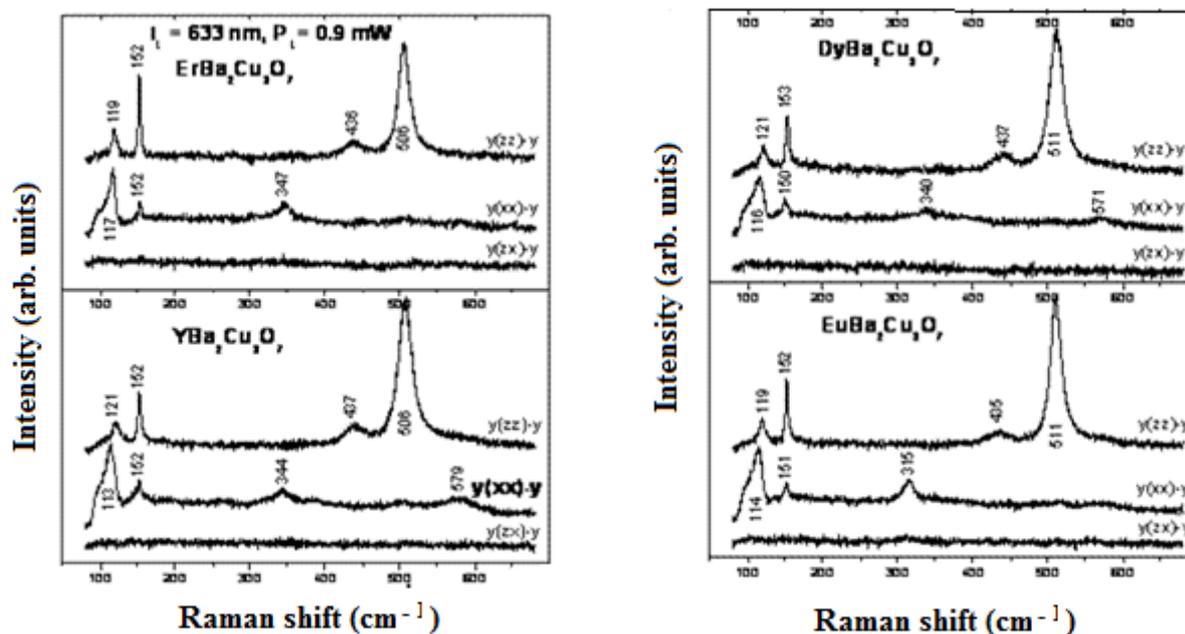


**Figure 2.** Absorption spectra of the complexes: Co (II)-EDTA (1), Co(III)-EDTA (2) and Cu(II)-EDTA (3) in sodium acetate-acetic acid buffer in the presence of silver;

$$C_{\text{Co(III)-EDTA}} = 4.20 \cdot 10^{-3} \text{ mol l}^{-1}; C_{\text{Cu(II)-EDTA}} = 4.90 \cdot 10^{-3} \text{ mol l}^{-1}; C_{\text{Co(II)-EDTA}} = 6,46 \cdot 10^{-3} \text{ mol l}^{-1} .$$

The oxygen content was also analyzed by Raman spectroscopy and the physical and chemical methods for its determination were compared.

The polarized Raman spectra obtained from  $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$  ceramics are shown in Fig. 3.



**Figure 3.** Polarized Raman spectra of  $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$  ( $R = \text{Er, Y, Dy, Eu}$ ) at room temperature. The laser wavelength, the power used and the configuration of the scattering (using the Porto notations) are indicated. For better viewing the spectra are shifted in vertical direction.

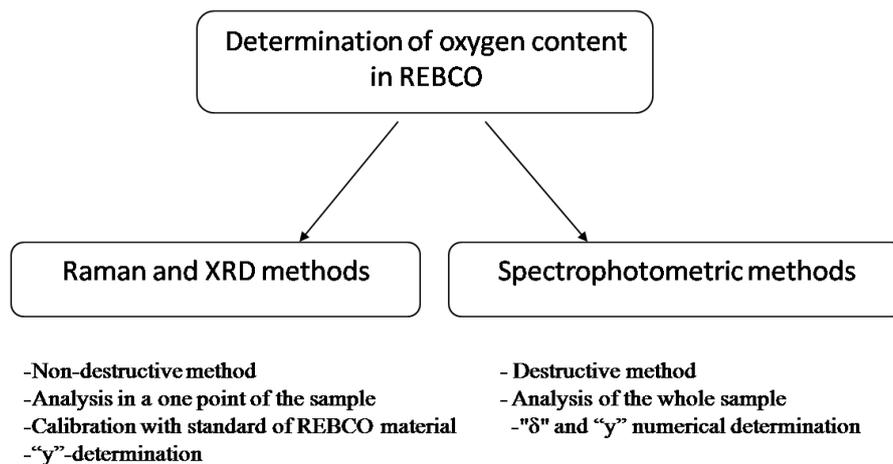
There are five lines in them, corresponding to the  $5 A_g$  modes allowed in the first-order (one-phonon) inelastic phonon scattering by the orthorhombic phase. All 5 modes are vibrations perpendicular to the Cu-O planes of Ba (near  $120 \text{ cm}^{-1}$ ), plane-Cu2 (near  $150 \text{ cm}^{-1}$ ), out-of-phase O2-O3 (near  $340 \text{ cm}^{-1}$ ), in-phase O2-O3 (near  $430 \text{ cm}^{-1}$ ) and apex O4 (near  $500 \text{ cm}^{-1}$ ), respectively. Raman spectroscopy is a sensitive tool for study of the  $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ , because the position and the relative intensity of the lines in different types of spectra strongly depend on the type of the rare earth as well on the oxygen content and the degree of the oxygen disorder in the planes of Cu-O chains [23-

26]. The most sensitive line to the ionic radius of the rare earth is the out-of-phase O2-O3 mode (also known as the “quasi  $B_{1g}$ -mode”, because in the tetragonal  $\text{RBa}_2\text{Cu}_3\text{O}_{6+x}$  it has  $B_{1g}$  symmetry). Its frequency increases from  $297 \text{ cm}^{-1}$  in the case  $R = \text{La}$  to  $350 \text{ cm}^{-1}$  for  $R = \text{Lu}$  [24-26]. This dependence can be seen in our spectra, too. The frequency of this line increases from  $315 \text{ cm}^{-1}$  (for  $R = \text{Eu}$ ) to  $347$  (for  $R = \text{Er}$ ). Dramatic changes in the spectra have been observed also with the change of the oxygen content. Whereas the O4 line in orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  ( $x \approx 0$ ) is near  $503 \text{ cm}^{-1}$ , in the tetragonal oxygen deficient  $\text{YBa}_2\text{Cu}_3\text{O}_{6+y}$  ( $y < 0.3$ ) this line is near  $473 \text{ cm}^{-1}$  [27]. Large changes in the relative intensities in

(zz) and (xx) spectra were observed for the modes of Ba, Cu<sub>2</sub>, and in-phase O<sub>2</sub>-O<sub>3</sub>, too [23, 27]. However, the early attempts to find simple quantitative dependence between the position of the high-frequency intensive O<sub>4</sub> mode and the degree of the oxygen deficiency failed. It was shown that in samples with intermediate oxygen content the profile of this line is complex superposition of lines with close but different frequency corresponding to domains with different oxygen content (in terms of coexisting phases they are the so called OI, OII and T phase) or to vibrations of O<sub>4</sub> atoms with different local environment [28]. From the spectra shown in Fig. 3, however, it is seen that the frequency of the O<sub>4</sub> mode is one of the highest ones, reported in the literature. On the other side, the attempts to fit the profile of the line near 500 cm<sup>-1</sup> with more than one Lorentzian failed. Therefore we can conclude that the oxygen content of RBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> in our samples is very close or equal to 7. Small doubts about existence of some small quantity of the oxygen vacancies in the Cu-O chains are the observation of a weak defect line near 570 cm<sup>-1</sup>, more clearly pronounced in the case of R = Y and Dy. We have to stress that although the Raman spectra of REBCO

are very sensitive to the oxygen content they cannot be used directly to determine numerically it.

Analytical control for the production of superconducting REBCO bulk samples is an important process step. The choice of the method for the determination of oxygen content depends from the specifics of the material, available equipment and the accuracy of determinations. Raman spectroscopy as well X-ray diffraction provide determining of the oxygen stoichiometry quickly and with operational comfort but the accuracy and the precision of the obtained results are not as good as the accuracy and precision of "y" determined by destructive methods. Physical methods determine the oxygen content in a small part of the material. In order to perform the analysis with destructive methods have to 1) take a representative sample and 2) to bring the sample in solution. Thus, the obtained results are more accurate and reliable. Moreover, only the destructive methods as titrimetric, spectrophotometric and coulometric methods can determine the non-stoichiometric oxygen content "δ". The difference between the oxygen determinations by both methods are summarized in Fig. 4.



**Figure 4.** Differences between the oxygen determination by spectrophotometry and Raman.

## Conclusions

A spectrophotometric method for oxygen determination in RBa<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> (R is rare earth element) superconductivity bulk samples was applied for the superconductive systems: R = Eu, Er and Dy. The method was optimized for determination of the oxygen content in these materials deposit on substrates. The silver ions in the substrates do not influence the determinations. All samples were also analyzed by Raman spectroscopy. The determination of the oxygen content by both methods shows that all samples are superconductivity with the oxygen content close to 7. The accurately "y" and "δ" values were calculated by the spectrophotometric method. The standard deviation of the δ- and y-coefficient results is 0.012. The reproducibility of the y-values in relative units

(sr) is 0.2%. Raman spectroscopy gives a qualitative estimation of the oxygen content. We suggest for analytical control of REBCO bulk samples in the practice to use the spectrophotometric method. It determines accurately the non-stoichiometric coefficient "δ".

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