Determination of the oxidizing ability of HTSC materials containing two elements with a variable degree of oxidation

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Abstract. The presence of mixed valence states of elements is supposed to be a common characteristic feature of the high- T_c superconductors, based on copper oxides. Methods have been suggested for the determination of Cu(III) in the Y–Ba–Cu–O ceramics and separate determination of two oxidants: Bi(V) and Cu(III), Tl(III) and Cu(III) in the corresponding materials. Compounds of Bi(V) oxidize in the ions of Mn(II) to MnO_4^- in the acidic medium. Active oxygen, bound to Cu(III) is isolated, not oxidizing Mn(II). MnO_4^- is titrated then with a solution of Fe(II) sulphate. For the determination of Tl(III) the sample is dissolved in the acid, Cu(III) is reduced to Cu(II) and Tl(III) is titrated with the hydroquinone solution. The compounds of Bi(V), Tl(III) and Cu(III), having high oxidation-reduction potentials can oxidize the complex Co(II)-EDTA to Co(III)-EDTA. The colour intensity of the latter is proportional to the content of Cu(III) or to the sum of Bi(V) and Cu(III) or Tl(III) and Cu(III). The content of Cu(III) in Bi- and Tl-containing materials is determined by the difference.

Keywords. Oxidizing ability; valence states of elements; titrimetry; spectrophotometry.

1. Introduction

Electrical and magnetic properties of HTSC materials depend, to a great extent, on the oxygen content in them. The correlation between the transition temperature T_c and the oxygen deficiency y has been found for all known oxide copper-containing superconductors. It is shown for example that at $y = 0$ for the system $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ T_c is maximal (92 K); with increase of y , T_c lowers and at $y = 0.6$ it is 22 K (Raveau *et al* 1988).

For the HTSC ceramics $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_2\text{O}_x$ T_c is 117 K at $y = 0$ and 99 K at $y = 0.36$ (Schilling *et al* 1988). The dependence between the superstoichiometric oxygen and T_c for the system Bi–Ca–Sr–Cu–O has also been established (Bohaček *et al* 1988).

It is generally recognized that the oxygen content in HTSC compounds is essentially higher than that which corresponds to the usual valence states for the elements of the composition. Thus, in $\text{YBa}_2\text{Cu}_3\text{O}_x$ high- T_c superconductivity appears only at $y > 6.5$. The problem of copper, bismuth, thallium and oxygen states has been discussed elsewhere. Some authors consider copper to be in a mixed valence state: +2 and +3. The data of X-ray electron spectroscopy (Boyce *et al* 1988; Jaeger 1989; Dobrotvorskaya *et al* 1988), X-ray absorption spectroscopy (Maeda *et al* 1987; Lengeler *et al* 1988) and other methods give evidence in favour of this assumption. According to the other model the electric neutrality of the compound Y–Ba–Cu–O is ensured by the presence of oxygen in an abnormal degree of oxidation –1, included in the complex $\text{Cu}^{2+} - \text{O}^-$ (Bianconi *et al* 1987). Some authors discuss the probability of existence of the complex $\text{Cu}^{2+} - \text{O}^\circ - \text{Cu}^{2+}$ (Khomski and Zvezdin 1988) or oxygen dimers O_2^{2-} (Dzyaloshinskii 1989) as well as Cu(I) (Sarma and Rao 1988).

Results of the physical methods of investigation do not allow us to solve the problem

of the valence states of Cu, Tl and Bi unambiguously. However, the presence of mixed valence states of elements is probably a common characteristic of the high- T_c superconductors based on copper oxides (Torardi *et al* 1988). Thallium and copper are supposed to be in the form: Tl(III) and Tl(I), Cu(III) and Cu(II) (Hewat *et al* 1988; Kikuchi *et al* 1989; Krasinkova and Moizhes 1989; Schilling *et al* 1989), Bi and Cu- in the form: Bi(III) and Bi(V), Cu(III) and Cu(II) (Bohaček *et al* 1988; Von Schnering *et al* 1988; Zandberger *et al* 1988). A number of analytical methods for the determination of labile oxygen (Watanabe *et al* 1988; Hornig *et al* 1989) and formal valence state of copper (Harris *et al* 1987; Novak *et al* 1989) have been suggested. Tang and co-authors (1988) showed that Cu(I) is absent in the HTSC ceramics $\text{YBa}_2\text{Cu}_3\text{O}_x$. We have experimentally found the absence of peroxide compounds in $\text{YBa}_2\text{Cu}_3\text{O}_x$ (Pantaler and Lebed 1989).

The most probable supposition is that the high oxidizing ability of the superconducting complex oxides is due to the presence of Cu(III) or chemically indistinguishable from its complex $\text{Cu}^{2+}-\text{O}^-$ as well as Bi(V) and Tl(III). Due to the supposed availability of two elements in different formal degree of oxidation in Bi- and Tl-containing materials: B(V) and Bi(III), Tl(III) and Tl(I), Cu(III) and Cu(II), the data obtained by some authors on the oxidizing ability of the said HTSC ceramics should not be attributed only to the presence of Cu(III). When the reactions of iodide and iron(II) are used for the estimation of the oxidizing ability of the HTSC ceramics (Rao *et al* 1988; Tarascon *et al* 1988) apart from Cu(III) or $\text{Cu}^{2+}-\text{O}^-$ an essential contribution into the spending of the reducer is made by Bi(V) and Tl(III). Our method for the determination of Cu(III) in the Y-Ba-Cu-O ceramics and separate determination of two oxidizers Bi(V) and Cu(III), Tl(III) and Cu(III) is as follows: Compounds of Bi(V) oxidize the ions Mn(II) to Mn_4^+ in the acidic medium. Active oxygen, bound with copper, is isolated from the solution without oxidizing Mn(II). Thus the permanganate formed is titrated with the solution of the More salt and Bi(V) content is determined. When determining Tl(III), the sample is dissolved in acidic medium; Cu(III) is reduced to Cu(II) with release of gaseous oxygen and Tl(III) ions are titrated with a solution of hydroquinone which is oxidized to *p*-quinone. The compounds Bi(V), Tl(III) and Cu(III) possessing high oxidizing-reducing potentials, are able to oxidize the complex Co(II) with EDTA with the formation of the complex Co(III) - EDTA, the intensity of colour of which is proportional to the content of Cu(III) or the sum of Bi(V) and Cu(III) or Tl(III) and Cu(III). The content of Cu(III) in the Bi- or Tl-containing materials is determined by the difference on account of the results of the separate determination of Bi(V) or Tl(III).

To find the total content of Bi, Tl and Cu as well as the rest cations of the base, X-ray fluorescence and complexometric methods are used.

2. Determination of Bi(V)

Ten ml of the HNO_3 (1:2) solution, 1 ml of that of MnSO_4 and 0.1 g of the ground sample are placed into a conical flask. The contents are mixed until a full dissolution of the sample, diluted with water to the volume 50 ml and titrated with 0.005 M solution of FeSO_4 the concentration of which is established on the day of application according to the solution of potassium bichromate. At the end of titration some drops

of 0.1% solution of the phenylanthranilic acid are added to the analysed solution and then titration is continued till the disappearance of a red-violet colour of the indicator.

3. Determination of Tl(III)

0.02...0.05 g of the sample is placed into a glass of the capacity of 50 ml and dissolved in 1 ml of the concentrated HNO_3 while heated. Fifteen ml of water is added to the obtained solution and titrated potentiometrically with 0.01 N solution of hydroquinone in the 0.05 M solution of HNO_3 using platinum and chlorum-silver electrodes till the jump of the potential. The hydroquinone solution is standardized with reference to potassium bichromate.

4. Determination of Cu(III) and total oxidizing ability of bismuth and copper, thallium and copper

Five ml of water, 2 ml each of the 0.2 M solutions of EDTA and CoCl_2 , 1 ml of the acetate buffer solution with pH 4.5 and 0.05...0.06 g of the sample are placed in a glass with 50 ml capacity having a ground-in stopper. The glass is put into a magnetic mixer, solution with a precipitate is stirred till the sample is fully dissolved (1.5...2 hr). The solution is then replaced into a measuring flask with a 50 ml capacity added with water till the marker. The optical density of the solution is measured in a 2 cm cell at 540 nm with respect to a solution of the checking sample containing the above mentioned reactants.

By calculations, according to calibration plots, constructed with the help of solutions with the known content of Bi(V), Tl(III) and Cu(III) with allowance for the previously found content of Bi(V) or Tl(III) the content of Cu(III) is determined. Ti_2O_3 , synthesized and analysed Bi_2O_5 , potassium ditelluratecuprate (III) are used as initial compounds for constructing the plots.

Relative standard deviations, when determining $n \times 10^{-5}$ M Cu(III) in the ceramics Y-Ba-Cu-O for 20...25 tests are 0.02...0.03, in Ti- and Bi-containing materials: 0.04...0.06; Bi(V): 0.02...0.05, Tl(III): 0.007...0.014.

The results of determination of the formal state of oxidation of Cu, Bi and Tl in some samples of the superconducting ceramics are given in table 1.

Table 1. HTSC ceramics composition. Experimental results.

System	Components ratio	Composition
Y-Ba-Cu-O	1:2:3	$\text{YBa}_2\text{Cu}_{2.04}^{\text{II}}\text{Cu}_{0.96}^{\text{III}}\text{O}_{6.98}$
Gd-Ba-Cu-O	1:2:3	$\text{GdBa}_2\text{Cu}_{2.50}^{\text{II}}\text{Cu}_{0.50}^{\text{III}}\text{O}_{6.75}$
Bi-Sr-Ca-Cu-O	1:1:1:2	$\text{Bi}_{0.88}^{\text{III}}\text{Bi}_{0.12}^{\text{V}}\text{SrCaCu}_{1.72}^{\text{II}}\text{Cu}_{0.28}^{\text{III}}\text{O}_{5.76}$
	2:2:1:2	$\text{Bi}_{1.81}^{\text{III}}\text{Bi}_{0.19}^{\text{V}}\text{Sr}_2\text{CaCu}_{1.66}^{\text{II}}\text{Cu}_{0.34}^{\text{III}}\text{O}_{8.36}$
	4:3:3:4	$\text{Bi}_{3.75}^{\text{III}}\text{Bi}_{0.25}^{\text{V}}\text{Sr}_3\text{Ca}_3\text{Cu}_{3.35}^{\text{II}}\text{Cu}_{0.65}^{\text{III}}\text{O}_{16.58}$
Tl-Ba-Ca-Cu-O	1:2:1.94:2.44	$\text{Tl}_{0.96}^{\text{III}}\text{Tl}_{0.04}^{\text{I}}\text{Ba}_2\text{Ca}_{1.94}\text{Cu}_{1.48}^{\text{II}}\text{Cu}_{0.96}^{\text{III}}\text{O}_{8.32}$
	0.5:2:2.66:4	$\text{Tl}_{0.47}^{\text{III}}\text{Tl}_{1.03}^{\text{I}}\text{Ba}_2\text{Ca}_{2.66}\text{Cu}_{3.73}^{\text{II}}\text{Cu}_{0.27}^{\text{III}}\text{O}_{9.52}$

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