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An Improved Coulometric Titration Method for Oxygen Content and Valence Determinations in Bismuth and Lead Cuprates

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A two-step coulometric titration procedure originally published for the determination of the average valences of both copper and bismuth in the bismuth based cuprate superconductors was modified in order to avoid the effects of an observed harmful side reaction. Furthermore, the improved method was found to be applicable to the analyses of lead containing materials as well. The first titration experiment, which consists of the reactions of Cu(III), Bi(V), and Pb(IV) with Cu(I) followed by an anodic oxidation of the excess Cu(I), reveals the oxygen content of the sample. In the second experiment the valences of bismuth and lead are distinguished from the Cu-valence by taking advantage of the reaction with Fe(II). The selectivities of the proposed wet chemical processes were studied using $YBa_2Cu_3O_z$, $BiNaO_3$, PbO_2, and Pb_3O_4 as reference materials for Cu(III), Bi(V), and Pb(IV), respectively. Additionally, the oxygen content and the average metal valences were determined in a single phase superconducting sample of $(Bi,Pb)_2Sr_2CaCu_2O_z$. © 1993 Academic Press, Inc.

Introduction

Owing to the crucial importance of the mixed valence state of copper on high T_c superconductivity several methods of chemical analysis, including iodometric titrations (*1*) and thermogravimetric reductions (*2*), have been adapted to establish the average Cu-valence in $YBa_2Cu_3O_{7-y}$. However, when multivalent metals of various kinds are simultaneously present, the Cu-valence and the valences of the other multivalent metals cannot be distinguished by these ordinary methods. Recently, Kurusu *et al.* (*3*) reported that the Cu- and Bi-valences were successfully separated and analyzed in $Bi_2Sr_2CaCu_2O_{8+y}$ by a coulometric technique involving two steps of titration. In the first experiment both Cu(III) and Bi(V) react with Cu(I), while in the second experiment the reaction scheme consists of a selective reduction of Bi(V) by Mn(II) and a subsequent determination of the produced permanganate by Fe(II).

In the experimental conditions of the above coulometric method, various chemical processes are thermodynamically possible. In the present study the different reactions occurring are demonstrated and the effects of an observed harmful side reaction are discussed. In order to improve the quantitativity and accuracy of the determinations, a modified analysis route, based on the selective reduction capability of Fe(II) instead of Mn(II) in the second titration experiment, is proposed. The oxidation power of Pb(IV) appears to be strong enough to oxidize both Cu(I) and Fe(II), thus suggesting that the proposed method could be applicable to analyses of lead-containing materials as well. The selectivities of the desired reactions are confirmed using simple reference materials for Cu(III), Bi(V), and Pb(IV), and finally, the oxygen content and

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the average metal valences are studied in a superconducting $(Bi,Pb)_2Sr_2CaCu_2O_z$ sample.

Experimental

In order to study the chemical reactivity of Cu(III), Bi(V), and Pb(IV), $YBa_2Cu_3O_z$, $BiNaO_3$ (Wako Pure Chemical Industries, Ltd., 80.0%), PbO_2 (Wako Pure Chemical Industries, Ltd., 95%), and Pb_3O_4 (High Purity Chemicals, 99.99%) powders were selected for reference materials. The superconducting $YBa_2Cu_3O_z$ reference was prepared in air by a conventional solid state reaction method and the oxygen content was established by iodometric titrations performed under nitrogen atmosphere in 5 *M* HCl solution. The $Na_2S_2O_3$ titrant (0.01 *M*) was standardized against known CuO samples.

The single phase superconducting (T_c = 83K) $Bi_{1.8}Pb_{0.2}Sr_2CaCu_2O_z$ sample was synthesized by a solid state reaction starting from a stoichiometric mixture of Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, and CuO. The starting material mixture was first calcined twice in air at 760°C for 10 hr, and then sintered in a nitrogen atmosphere at 810°C for 30 hr.

The equipment used in the coulometric measurements was essentially similar to that described in Ref. (*3*). The titrations were carried out at room temperature under flowing nitrogen atmosphere. The 1 *M* HCl cell solution was freed from dissolved oxygen by bubbling nitrogen gas through it for 30 min, and the initial redox power of the cell was standardized by performing pretitrations each time with small amounts of the corresponding reducing agents: CuCl (High Purity Chemicals, 99.99%) and $FeCl_2 \cdot 4H_2O$ (High Purity Chemicals, 99.9%). Before the actual analyses, blank titrations were carried out to check the Cu(I) and Fe(II) contents of these reductants. Other chemicals used in the experiments were $MnCl_2 \cdot 4H_2O$ (High Purity Chemicals, 99.9%), CuO (High Purity Chemicals, 99.9%), Bi_2O_3 (High Purity Chemicals, 99.99%), and PbO (High Purity Chemicals, 99.9%). The coulometric titration of Cu(I) was performed at a constant current of 5 mA until the potential of the Ag/AgCl indicator electrode reached 950 mV. The corresponding values in the case of the anodic oxidation of Fe(II) were 3 mA and 810 mV.

Results

The oxygen contents and distinct metal valences in bismuth and lead cuprates can be determined by two redox experiments where coulometric back-titrations of the reducing agents are applied as final analysis steps. The sum of the extra oxidation states above +II for copper, +III for bismuth, and +II for lead and thus the total oxygen content of the sample is obtained in the first experiment by reducing all the high valent metal ions by Cu(I). For the separation of the Cu-valence from the valences of bismuth and lead the direct reduction of Bi(V) and Pb(IV) by Fe(II) instead of the two step reaction scheme proposed by Kurusu *et al.* (*3*) was found to give more reliable results. Namely, if Bi(V) and Pb(IV) are first reduced in HCl solution by Mn(II) followed by the determination of the produced MnO_4^--ions with Fe(II), some permanganate is consumed in a slow but yet noticeable reaction between MnO_4^-- and Cl^--ions before the Fe(II)-compound is added to the cell. The effect of this harmful side reaction on the observed Bi- and Pb-valences depends on the dissolution time allowed between the additions of the sample and Fe(II)-reductant (Fig. 1). Although the tendency of permanganate to oxidize chloride is known to be minimized in the presence of Mn^{2+}-ions, the results obtained for the $BiNaO_3$ reference material (sample size 20–50 mg) by the sequent Mn(II)/Fe(II)-reduction method (0.2 *M* Mn^{2+} and 1 *M* HCl) revealed that a dissolution time of 15 min was enough to decrease the detected Bi(V) amount by ca. 50%. In the case of superconducting samples the effect of the reaction between MnO_4^-- and Cl^--ions may, how-

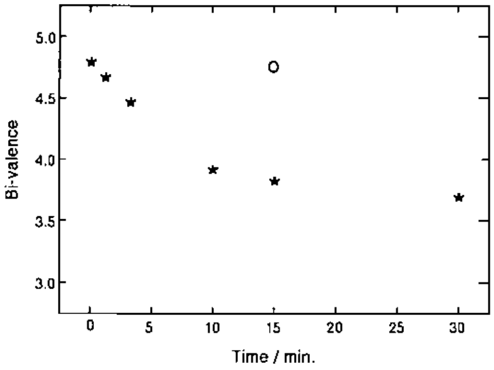

FIG. 1. The effect of the dissolution time between the addition of the sample and of the Fe(II)-reductant on the observed Bi-valence value in $BiNaO_3$ when analyzed by the sequent Mn(II)/Fe(II)-reduction method (*3*) in 1 *M* HCl (*) and 1 *M* H_2SO_4 (○) electrolytes.

ever, be less detrimental since the Bi(V) contents and thus the produced permanganate concentrations are usually lower. From the results presented in Fig. 1 it can be further seen that sulfuric acid would in principle be a suitable cell solution for the Mn(II)/Fe(II) reduction, as it has no action upon permanganate in dilute solution. However, H_2SO_4 is not an optimal solvent for high T_c superconductors.

In the following two sections the proposed novel modification of the original coulometric titration method is described along with the experimental results on the $YBa_2Cu_3O_z$, $BiNaO_3$, PbO_2, and Pb_3O_4 references demonstrating the selectivities of the desired chemical reactions. All the results of the different titration experiments for the reference materials are also summarized in Table I. The reported results are average values of several repeated titrations. An error limit of ±0.01 for the valence values was observed between parallel experiments. The results obtained for the $Bi_{1.8}Pb_{0.2}Sr_2CaCu_2O_z$ sample are presented in the third section.

Determination of the Total Oxidation Power

In the first titration experiment the sum of Cu(III), Bi(V) and Pb(IV), and thus the oxygen content of the sample, is determined according to Eqs. (1), (2),and (3) by dissolving the sample (50–150 mg) in 1 *M* HCl containing ca. 0.002 *M* CuCl. The excess of Cu(I) is then back-titrated by an anodic oxidation as indicated in Eq. (4):

$$Cu^{3+} + Cu^{+} \rightarrow 2\,Cu^{2+} \quad (1)$$

$$BiO_3^- + 2\,Cu^{+} + 4\,H^{+} \rightarrow BiO^{+} + 2\,Cu^{2+} + 2\,H_2O \quad (2)$$

$$Pb^{4+} + 2\,Cu^{+} \rightarrow Pb^{2+} + 2\,Cu^{2+} \quad (3)$$

$$Cu^{+}\,(\text{excess}) \rightarrow Cu^{2+} + e^{-}\ \text{coulometry} \quad (4)$$

According to thermodynamics, Cu(III), Bi(V), and Pb(IV) all can react with water or Cu(I). From the titration data given in Table I, it is, however, clearly seen that Cu(I) is oxidized selectively at least by trivalent copper and tetravalent lead, as the results obtained for the $YBa_2Cu_3O_z$ reference material by the iodometric (z = 6.87) and coulometric (z = 6.86) methods are in reasonably good agreement and the observed Pb-valences in the reference lead oxides (+4.01 for PbO_2 and +2.68 for Pb_3O_4) are equal to the theoretical values within the estimated error limits. In the case of bismuth the obtained low valence value (+4.82) compared to the theoretically expected Bi-valence value of +5.00 in pure $BiNaO_3$ does not either necessarily mean that the reaction between Bi(V) and Cu(I) is unquantitative, since alkali bismuthates are commonly impure and poorly characterized.

Determination of the Bi- and Pb-Valences

In the second experiment the sample is dissolved in 1 *M* HCl containing $FeCl_2 \cdot 4H_2O$ (ca. 0.001 *M*) resulting in reactions (6) and (7) between Fe(II) and Bi(V) or Pb(IV). The average valences of bismuth and lead can then be determined by a coulometric titration of the excess of Fe(II) (Eq. (8)):

$$4\,Cu^{3+} + 2\,H_2O \rightarrow 4\,Cu^{2+} + O_2 + 4\,H^{+} \quad (5)$$

$$BiO_3^- + 2\,Fe^{2+} + 4\,H^{+} \rightarrow BiO^{+} + 2\,Fe^{3+} + 2\,H_2O \quad (6)$$

TABLE I

TITRATION RESULTS FOR THE REFERENCE MATERIALS

Reference material	Titration method (sequence of addied reactants)	Cu-Valence	Bi-Valence	Pb-Valence
$YBa_2Cu_3O_z$	Iodometric ($KI + YBa_2Cu_3O_z + Na_2S_2O_3$)	+2.247		
	Experiment 1 ($CuCl + YBa_2Cu_3O_z$)	+2.242		
	Experiment 2 ($Bi_2O_3 + PbO + FeCl_2 + YBa_2Cu_3O_z$)	+2.000		
	Reverse Experiment 1 ($YBa_2Cu_3O_z + CuCl$)	+2.004		
$BiNaO_3$	Experiment 1 ($CuCl + BiNaO_3$)		+4.824	
	Experiment 2 ($CuO + FeCl_2 + BiNaO_3$)		+4.810	
PbO_2	Experiment 1 ($CuCl + PbO_2$)			+4.005
	Experiment 2 ($CuO + FeCl_2 + PbO_2$)			+3.994
Pb_3O_4	Experiment 1 ($CuCl + Pb_3O_4$)			+2.684
	Experiment 2 ($FeCl_2 + Pb_3O_4$)			+2.667

$$Pb^{4+} + 2\,Fe^{2+} \rightarrow Pb^{2+} + 2\,Fe^{3+} \qquad (7)$$

$$Fe^{2+}\,(\text{excess}) \rightarrow Fe^{3+} + e^{-}\ \text{coulometry} \qquad (8)$$

Tetravalent lead of PbO_2 and Pb_3O_4 reacted quantitatively with Fe^{2+}-ions (Table I), while for Cu(III) the reaction with water (Eq. (5)) is obviously preferable; since no Fe(II) was consumed when $YBa_2Cu_3O_z$ was analyzed (observed Cu-valence +2.00) it is evident that neither the evolved oxygen reacts with Fe^{2+}-ions. The fast and complete reaction between Cu(III) and H_2O was also verified with a reverse titration experiment 1 by dissolving the Cu(III) reference material in the cell before CuCl. No Cu(III) was observed in that case either. Pentavalent bismuth was also found to react with water very fast as long as no Fe^{2+}- or Cu^{+}-ions were present. On the other hand, the rate of the reaction between Pb(IV) and H_2O could not be studied as the lead oxides used dissolve very slowly. The Bi-valence value of +4.81 observed for $BiNaO_3$ in the second experiment is essentially equal to the result of the first titration experiment, thus strongly suggesting that the real Bi(V) concentration in the used $BiNaO_3$ powder is only about 90% of the theoretical content, and furthermore, that Bi(V) reacts quantitatively with both Cu(I) and Fe(II). Finally, as the studied $YBa_2Cu_3O_z$, $BiNaO_3$, and PbO_2 solutions also contained Bi^{3+}-, Pb^{2+}-, and Cu^{2+}-ions, respectively (Table I), the obtained results confirm further than in the experimental conditions concerned Cu(III) does not oxidize Bi(III) or Pb(II) and Cu(II) is not oxidized by Bi(V) or Pb(IV).

Studies on the (Bi, Pb)$_2$Sr$_2$CaCu$_2$O$_z$ Sample

The analytical results of the first experiment for the $Bi_{1.8}Pb_{0.2}Sr_2CaCu_2O_z$ sample establish that the oxygen content z is 8.10 ± 0.01. According to the results of the second experiment the Cu-valence was calculated to be +2.10, but for bismuth and lead only an average valence value of +3.00 could be determined. However, it is noticeable that this observed (Bi,Pb)-valence value cannot be achieved without mixed valent state of at least one of these two metals.

Discussion

The first experiment in the coulometric titration technique of Kurusu *et al.* (*3*) was found to be applicable, besides bismuth superconductors, also to the oxygen content analyses of lead and yttrium cuprates. In the case of $YBa_2Cu_3O_z$ the agreement of the results obtained from the coulometric and iodometric titrations was confirmed. The quantitativeness of the reaction between Pb(IV) and Cu(I) was verified using PbO_2 and Pb_3O_4 as reference materials for tetravalent lead.

Due to the observed harmful side reaction between MnO_4^-- and Cl^--ions in experiment 2 the direct reduction of Bi(V) and Pb(IV) by Fe(II) instead of the two step Mn(II)/Fe(II) reduction proposed earlier (*3*) was considered to give more reliable valence values for the metals. Although the reaction between Cu(III) and Fe(II) is occasionally adapted to analyze oxygen contents in high T_c superconductors (*4*, *5*), the Fe^{2+}-concentrations used have generally been high and the oxygen content values obtained thereof quite low. The results of the present study for the $YBa_2Cu_3O_z$ reference material confirm that the Fe^{2+}-concentration in the proposed coulometric technique is too low to compete successfully with the O_2-evolution.

The observed Bi(V) content in $BiNaO_3$ was found to be ca. 10% lower than the theoretical value. The facts that (i) the manufacturer confirms only 80% purity for the used powder and (ii) equal valence values were obtained in both experiments, however, strongly suggest that the determinations are quantitative also for Bi(V). Even if the analyses tend to give too small valence values for bismuth, the equally large systematic errors in both experiments would be counteracted when the most important Cu-valences are calculated.

When the studied sample contains both bismuth and lead the distinct Bi- and Pb-valences cannot be detected by the proposed method, but as a result of experiment 2 the average (Bi,Pb)-valence is observed. In fact, according to the strong evidence given by Scheurell *et al.* (*6*), Bi(V) oxidizes Pb(II) to Pb(IV) during acidic dissolution and no chemical method which involves the dissolution of the sample can distinguish the individual Bi- and Pb-valences.

A critical question, common for all solution based valence studies, is how well the solid state properties, e.g., the metal valences, are maintained upon dissolving the material. At least the results of the studies on the $(Bi,Pb)_2Sr_2CaCu_2O_z$ sample confirm that by the proposed method noninteger valence values can be obtained for more than one metal in the same sample. For the further proof the importance of various comparative characterization methods as well as studies on sample series with gradually changing properties is emphasized.

Summary

The oxygen contents in the bismuth and lead cuprates as well as in the yttrium based superconductors can be determined with high reliability and precision by a simple wet chemical redox experiment using CuCl as a reducing agent and applying coulometric titration of the excess Cu(I) as a final analysis step. This was demonstrated in the case of $YBa_2Cu_3O_z$ by the reproducibility of at least ± 0.01 in z and by the reasonably good agreement between the results obtained from the coulometric and iodometric titrations. Furthermore, as far as the solid state properties are considered to be maintained during dissolution, the crucial Cu-valences can be distinguished from the Bi- and Pb-valences by taking advantage of the selective oxidation capability of Fe(II).

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