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On the Determination of Hole Concentration and Oxygen Stoichiometry in Thallium Cuprate Superconductors

T. S. KRISHNAMOORTHY, N. MAHADEVAN, AND S. S. DESAI

Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay-400 094, India

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The utility and limitation of the wet chemical methods for the determination of hole concentration and oxygen stoichiometry in thallium cuprate high T_c compounds have been evaluated.

Introduction

The hole concentration and oxygen stoichiometry in high T_c oxides such as 123 oxides and Bi-based oxides have been determined usually by iodometric methods (*1–3*), based on Cu^{+3} content and assuming metal stoichiometries. However, problems arose when these direct iodometric methods were applied to thallium-based compounds, mainly due to the reduction of Tl^{+3} simultaneously with Cu^{+3}. Manthiram and co-workers (*4, 5*) determined separately (a) Tl stoichiometry and (b) the total oxidizing power (due to Tl^{+3} and Cu^{+3}) of the samples by direct iodometry. Assuming all Tl to be present as Tl^{+3}, they calculated the oxygen content of the sample. Gopalakrishnan *et al.* (*6*) reported a CCl_4 extraction–iodometric method, in which the bromine liberated due to the reduction of Cu^{+3} to Cu^{+2} is extracted and estimated iodometrically. In this, the reduction of Tl^{+3} does not take place. Subsequently, Manthiram *et al.* (*7*) have criticized the method of Gopalakrishnan *et al.* The present authors have also been working simultaneously on similar lines, and this communication gives a critical appraisal of both of these methods, their limitations, and probable use.

Experimental

Our extraction method is similar to that of Gopalakrishnan *et al.*, except that the oxide samples were weighed directly into separating funnels and dissolved in ice-cold 1 : 1 HBr, so as to avoid any loss of bromine due to transfer, washing, etc. The combined organic extracts after addition of excess KI solution were titrated with standard thiosulfate, without addition of starch (*8*). For direct iodometric titrations, the modified Appelman *et al.*'s method (*2, 3*) in the presence of citrate was used.

Results and Discussion

The standard method (*9*) used by Manthiram *et al.* will no doubt give unambiguously

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TABLE I

OXYGEN CONTENT IN $TlCa_2Ba_2Cu_3O_x$

% Tl assumed as		
Tl^{+3}	Tl^{+}	x
100	0	8.528
80	20	8.525
50	50	8.524
0	100	8.528

the total Tl content of the specimens irrespective of its valency state. The use of direct iodometry will give the total oxidizing power of the specimen, due to both Tl^{+3} and Cu^{+3}. They calculated the oxygen content (oxygen stoichiometry) assuming all Tl to be present as Tl^{+3}. We would like to point out that, for a given titre value and Tl content, the calculations will lead to the same oxygen content, even if Tl is distributed between Tl^{+3} and Tl^{+} states in any proportion. This is exemplified in Table I for one of our specimens. Thus it is possible to unambiguously calculate the oxygen content by this approach, if the purpose is only to obtain the molecular stoichiometries. However, problem arises when one tries to calculate the hole concentration from these data, particularly when Tl is distributed in both valence states. Manthiram *et al.* calculated the hole concentration in single-layer Tl compounds, where they had reason to believe Tl to be present only as Tl^{+3}. Though theoretically this is unexceptional, it has the practical limitation of any other indirect method, since the titre due to Cu^{+3} is only a small fraction of the total titre due to Cu^{+3} and Tl^{+3}; e.g., in the case of the data of Manthiram *et al.* (Table I, Ref. (*7*)), for $TlBaLaCuO_5$ and $TlBa_{1.4}La_{0.6}CuO_5$, the titre value due to the holes will be only 0.6 and 10.7%, respectively, of the total titre value. Similar is the case with samples analyzed in our laboratory, one example being the titre value of Cu^{+3} being about 0.6% of the total titre in a sample of $TlCa_2Ba_2Cu_3O_{8.5}$. As the hole concentration decreases lower and lower, determining the hole concentration, which is a minor constituent, indirectly by difference is not preferrable, if a direct method is available.

The extraction of bromine, liberated due to reduction of Cu^{+3} to Cu^{+2} during dissolution in HBr and estimating it iodometrically, can give the hole concentration directly, as Tl^{+3} does not get reduced under those conditions. Experimentally it was found that the formation and presence of Br_3^- ion impedes the extraction, and therefore the extraction increases with the decrease in HBr concentration. Our work established that three extractions are needed to get practically quantitative recovery when the acidity is about 0.5 M HBr at the extraction stage. Gopalakrishnan *et al.* have not specifically pointed out the importance of acidity and the number of extractions.

They have assumed implicitly that Tl does not interfere in the extraction method. Table II gives our experimental data on a 123 compound along with the effect of addition of Tl to the same. Extraction procedure is shown to give quantitative recovery of bromine on this sample (to within 5%), but there is a negative linear interference due to Tl. This can be attributed to the oxidation of Tl^{+} present by the bromine liberated *in situ* (Tl_2O_3 used in this study titrated to only 93% Tl^{+3} by conventional iodometry). This was further confirmed using thallous carbonate ($Tl_2CO_3 \geq 98.5\%$). When Tl^{+} was treated with HBr, solid TlBr separated. Addition of standard $KBrO_3$ to this resulted in the dissolution of TlBr. Table III shows the consumption of bromine in this reaction, confirming the oxidation of Tl^{+} to Tl^{+3} by the nascent bromine liberated *in situ*. Thus, our experiments agree with the criticism of Manthiram *et al.* (*7*) about the extraction method. In thallium cuprates, when Tl is present in Tl^{+3} and Tl^{+} states, the nascent bromine liberated by the reduction of Cu^{+3}

TABLE II

EXTRACTION ANALYSIS OF $YBa_2Cu_3O_x$

Serial no.	Compound	wt. (mg)	Method	mmol of Cu^{+3} per g of sample		% recovery in extraction method
1.	$YBa_2Cu_3O_x$	40	Direct iodometry	1.33 1.30 1.34 1.31	1.32	
2.	-do-	-do-	Extraction	1.26 1.25	1.26	100
3.	-do- + Tl_2O_3	30 to 35 + 12 to 14	-do-	1.20 1.22 1.07 1.18	1.17	92.9
4.	-do-	30 to 35 + 23	-do-	1.13	1.13	89.7
5.	-do-	30 to 35 + 35 to 40	-do-	1.04 1.06	1.05	83.3

will oxidize *in situ* the Tl^+. The titre obtained will thus represent the net bromine left after the reduction of Cu^{+3} and the *in situ* oxidation of Tl^+. It is also possible that if the concentration of $Tl^+ \geq 2\ Cu^{+3}$, net titre can even be zero. This is the major limitation of the extraction cum iodometric method.

However, when there is a reason to believe that Tl is present as Tl^{+3} (as taken by Manthiram *et al.* in single Tl layer compounds), extraction method can be used, without the above limitation, in spite of multiple extractions to achieve quantitative recovery. As a direct method of estimating hole concentrations, this is superior to that of Manthiram's indirect approach of calculating a small quantity of Cu^{+3} by difference from a significantly large experimental titre due to Tl^{+3}.

TABLE III

OXIDATION OF Tl^+ TO Tl^{+3} BY BROMINE

Tl_2CO_3 taken (mg)	Tl^+ in the specimen (mg)	Tl^+ in the specimen (μmol)	Bromine required for $Tl^+ \rightarrow Tl^{+3}$ (μmol)	Bromine actually consumed (μmol)
5.0	4.36	21.3	42.6	44.7
10.3	8.98	43.9	87.8	74.2
18.3	16.00	78.1	156.2	142.4

Table IV gives the results on some thallium cuprates by the extraction procedure. In single Tl layer cases, the hole concentrations, expressed here as Cu^{+3} and Cu^{+2}, are valid. In the double Tl layer cases, the values are at best the lower limit of hole concentration and can be used only as an indicator of batch-to-batch variations.

In conclusion, Manthiram *et al.*'s approach of separate Tl estimation and direct iodometry of total oxidizing power can give the oxygen content in all cases unambiguously. When Tl is present in both Tl^{+3} and Tl^+ states, neither this method nor the extraction method will give hole concentration. Both methods can give hole concentration only if Tl is present wholly as Tl^{+3}, and in such cases, the extraction method

TABLE IV

ANALYSIS OF THALLIUM CUPRATES BY THE EXTRACTION METHOD

S. no.	Compound[a]	mmol of Cu^{+3} per g of sample		Stoichiometry of Cu as	
				Cu^{+3}	Cu^{+2}
1.	$TlCa_2Ba_2Cu_3O_x$	0.33 0.35	0.34	0.30	2.70
2.	-do- (Different batch)	0.23		0.20	2.80
3.	-do-	0.35 0.36	0.36	0.32	2.68
4.	$Tl_2CaBa_2Cu_2O_x$	0.20 0.22	0.21	0.21	1.79
5.	-do- (Heated under argon)	0.29 0.27	0.28	0.27	1.73
6.	-do- (1-yr-old deteriorated)	0.18 0.16	0.17	0.17	1.83
7.	-do- (Different batch)	0.13 0.13	0.13	0.12	1.88

[a] Sample weight = 50–100 mg.

is superior experimentally, as this gives a direct estimate of the hole concentration. This study emphasises the need to overcome these limitations.

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