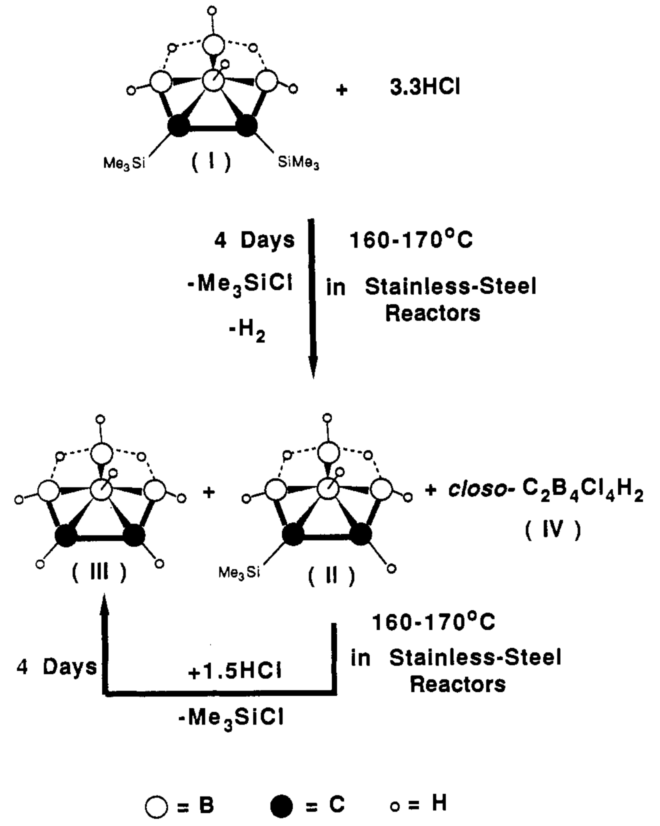
Scheme I



of I to HCl was 1:0.9, compound II was produced in 80% yield in addition to Me_3SiCl and H_2.

Infrared spectra and ^1H, ^{11}B, and ^{13}C NMR spectra of both II and III are identical with their published spectra.[2a,3,5] Compound IV was characterized by its ^1H, ^{11}B, ^{13}C, and ^{35}Cl pulse Fourier transform NMR and IR spectra.[6]

It is important to note that the ratio of reactants in Scheme I determines the formation of either one particular carborane or a mixture of several carborane products and their respective yields. Evidently, a large excess of HCl in Scheme I produced IV in that all the B–H bonds are chlorinated, whereas an insufficient quantity of HCl yields mainly mono(trimethylsilyl)-substituted carborane (II). However, for the high-yield preparation of the parent C_2B_4 carborane (III) the ideal molar ratio between I and HCl was found to be 1:3.3.

The new synthetic route described in this investigation is of extreme interest for the following reasons: (i) this is the method of choice over the existing method of preparation of 2,3-dicarba-*nido*-hexaborane(8) (III), which involves the gas-phase pyrolysis of a mixture of HC≡CH and B_5H_9; (ii) the reaction avoids the utilization of large-volume gas bulbs and Lewis bases and the necessity of handling the volatile flammable and explosive pentaborane–acetylene mixture; (iii) it does not result in the formation of a complex mixture of carboranes under specific conditions and hence eliminates the necessity of separating products by gas chromatography; and (iv) it could produce III in gram quantities since its precursor (I) is routinely prepared in multigram quantities.

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(6) FT NMR data (neat liquid): ^1H NMR (relative to external Me_4Si) δ 1.65 [s (br), 2 H, cage CH]; ^{11}B NMR (relative to external $BF_3{\cdot}OEt_2$) δ 62.76 [s, 4 B, basal B–Cl]; ^{13}C NMR (relative to external Me_4Si) δ 14.88 [d of q (br), cage CH, $^1J(^{13}C-^1H) = 181.4$ Hz, $^1J(^{13}C-^{11}B) = 65$ Hz]; ^{35}Cl NMR (relative to external $NaCl/D_2O$) δ 299.7 [s (br), cage B–Cl]. IR data (gas phase at 40 Torr vapor pressure): 2990 (m, br), 2965 (sh) [ν(C–H)], 1380 (s, br), 1308 (w, s), 1303 (m, s), 1260 (sh), 1200 (w), 1073 (m, br), 1050 (w), 1015 (s, br), 945 (w, br), 905 (m, br), 830 (s, br), 765 (s, br), 625 (sh), 570 (w, br), 529 (s, br) cm^{-1}. Mass spectrum: since the compound IV is extremely sensitive to air and/or moisture even in trace quantity, it decomposed in the mass spectrometer.

Oxygen Content of Superconducting Perovskites, $La_{2-x}Sr_xCuO_y$ and $YBa_2Cu_3O_y$

Sir:

Since the recent discovery of high superconducting transition temperatures (T_c), first in $La_{2-x}(Ba,Sr)_xCuO_y$ ($T_c \simeq 30$–40 K) and second in $YBa_2Cu_3O_y$ ($T_c \simeq 90$ K), the superconducting properties of these oxides have been generally considered to be dependent on their oxygen content.[1,2] While acknowledgment has been made of the importance of oxygen stoichiometry, however, most studies of these materials to date have neglected chemical analyses, although articles are now beginning to appear that attempt to correlate analyzed oxygen content with variations in electrical transport properties.[3] The superconducting properties of $YBa_2Cu_3O_y$ are influenced by an additional factor, only recognized very recently, that relates to a tetragonal-to-orthorhombic phase transition near ~700 °C. Either of the two pure phases or a two-phase mixture can be obtained at room temperature, depending on the high-temperature O_2 annealing procedures and the cooling rates.[4] The two phases, each of composition $YBa_2Cu_3O_y$ (but generally with different values of y), have considerably different normal-state and superconducting properties: the orthorhombic phase is the ~90 K superconductor, whereas the tetragonal phase is either a semiconductor or at best a lower T_c superconductor. The occurrence of a two-phase mixture thus considerably complicates the correlation of properties with oxygen content.

Since in the composition $YBa_2Cu_3O_y$ Y and Ba have fixed oxidation states of +3 and +2, respectively, a direct relationship exists between the Cu(II):Cu(III) ratio and the oxygen stoichiometry: if the compound contains only Cu(II), $y = 6.5$, whereas if it contains all Cu(III), $y = 8.0$. In classical studies of Cu(III) compounds such as $KCuO_2$, the Cu(III) content has been determined by iodometry or by hydrogen reduction.[5-7] Hydrogen reduction has thus far been the principal analytical procedure used

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for oxygen determination in the $YBa_2Cu_3O_y$ materials,[3] although iodometric procedures have recently been applied.[8] Neutron diffraction measurements also have yielded oxygen content along with structural details from refinements of intensity profiles.[2,9,10] In this communication, we present a modification of the iodometric method that is simple to apply and is particularly suited to analyses of the $La_{2-x}Sr_xCuO_y$ and the $YBa_2Cu_3O_y$ materials. We then apply this procedure to examine the oxygen content of $YBa_2Cu_3O_y$ in relation to its crystallographic and superconducting properties.

Synthesis. Samples of $La_{2-x}Sr_xCuO_y$ were synthesized by dissolving weighed amounts of ignited La_2O_3 and $SrCO_3$ along with Cu shot (all reagent grade) in nitric acid, evaporating the solution to dryness, and heating the mixture to 400 °C. The resulting powders were repeatedly ground and fired in air at 1000 °C. X-ray powder diffraction patterns showed only the expected orthorhombic phase of La_2CuO_y and the tetragonal phase for the Sr-doped compound.[9]

Samples of the $YBa_2Cu_3O_y$ materials were synthesized by the pH-adjusted carbonate coprecipitation route, as previously described.[4a] We have previously reported[4a] that the calcined materials are black, finely grained powders which are virtually pure orthorhombic-phase $YBa_2Cu_3O_y$, with only trace amounts of the impurities Y_2BaCuO_5 and CuO, as detected by X-ray powder diffraction patterns.[4a] For resistivity measurements, pressed pellets of the calcined materials were further annealed at 900 °C under a flowing oxygen atmosphere. Rapid air quenching of the annealed pellets from temperatures >700 °C produced an essentially pure tetragonal phase. Slow cooling below 700 °C over several hours under an O_2 atmosphere produced an essentially pure orthorhombic phase. Oxygen variations in the ceramic pellets of the orthorhombic phase were achieved by changes in the rate of cooling. X-ray powder diffraction patterns again indicated only trace amounts of the Y_2BaCuO_5 and CuO impurities.

Analysis of Cu(III). In the conventional iodometric method,[11] a Cu(II)–Cu(III) material is dissolved in an acidic iodide solution, resulting in reduction of all Cu species to solid copper(I) iodide. Thus, the titer represents the sum of total Cu plus Cu(III). Furthermore, in a medium of sufficient acidity to dissolve highly refractory materials such as $YBa_2Cu_3O_y$ at a reasonable rate, serious errors can result from Cu-catalyzed oxidation of I^- by atmospheric oxygen. The first of these two problems can be circumvented by carrying out the titration in the presence of citrate, which complexes Cu(II) and prevents its further reduction.[12] The second problem can be minimized by dissolving the material in ~4.4 M HBr and converting the Br_2 formed by reduction of Cu(III) to I_2 by subsequent reaction with I^- at a much lower acidity. The procedure is as follows.

An accurately weighed sample containing about 0.2 mmol of Cu is treated with 2 mL of ice-cold ~4.4 M HBr, made by 1:1 dilution of commercial 48% HBr, in a 4-mL vial having a Teflon-lined screw cap and containing a small Teflon-coated magnetic stirring bar.[13] The capped mixture is warmed to room temperature and stirred for at least 10 min. It is then transferred quantitatively to a 50-mL Erlenmeyer flask containing 20 mL of ice-cold 0.2 M KI and enough concentrated NH_3 to neutralize all but about 1 mmol of the added acid.[14] The solution in the flask should be stirred gently during the addition. The 4-mL vial and transfer pipet are washed twice with 2-mL portions of 2 M KBr. Five milliliters of 1 M sodium citrate is then added to the flask, and the solution is brought to room temperature and stirred until dissolution of the CuI precipitate is complete.[15] The iodine present is titrated with standardized 0.1 M sodium thiosulfate, with use of a 2.5-mL piston-displacement microburet. When the solution begins to change color, 2 drops of 1% aqueous amylose is added, and titration is continued until the dark blue amylose–iodine color changes to pale blue.[16]

Table I. Cu(III) Iodometric Analyses of Copper Oxide Superconducting Phases

compd	mass of sample, mg	amt of Cu(III), μmol	y^a
La_2CuO_y	78.41	2.6	4.007
	85.17	3.1	4.007
	70.87	2.2	4.006
$La_{1.85}Sr_{0.15}CuO_y$	79.50	27.8	3.994
	70.28	24.9	3.995
	72.10	25.2	3.995
$YBa_2Cu_3O_y{}^b$	38.84	48.6	6.916
	37.96	47.2	6.914
$YBa_2Cu_3O_y{}^c$	34.52	0.1	6.501
	42.91	0.0	6.500
$YBa_2Cu_3O_y{}^d$	40.00	53.2	6.942
	41.70	54.1	6.931
	38.00	49.5	6.933
	39.10	51.0	6.934

[a] Assumes metal composition given in first column. The oxygen coefficient y of an oxide $A_aB_bCu_cO_y$, where A is a rare earth and B is an alkaline earth, may be calculated from the titration result by means of the formula

$$y = (\alpha E + \beta)/(2 - 16E)$$

where

$$E = \text{mol of } S_2O_3{}^{2-} \text{ used/g of sample}$$
$$= \text{mol of Cu(III)/g of sample}$$
$$\alpha = aM_A + bM_B + 63.54c$$
$$M_A, M_B = \text{molar masses of metals A and B, respectively}$$
$$\beta = 3a + 2b + 2c$$

[b] Orthorhombic phase. [c] Quenched tetragonal phase. [d] Orthorhombic phase prepared from high-purity oxide powders; sample showed no trace of impurities such as CuO.

Since the HBr solution usually contains some bromine, a blank correction is required. This is best estimated by carrying out the entire procedure in the absence of the oxide sample. The amount of ammonia should still be adjusted to neutralize all but 1 mmol of the added acid. The thiosulfate titer of the blank should be subtracted from the titers of the actual samples. In our experiments the blank was between 0.5 and 3.9 μmol of thiosulfate. The corrected thiosulfate titer gives the amount of Cu(III) in the sample. If the metal stoichiometry is known, e.g., 1:2:3 for Y:Ba:Cu, the oxygen coefficient may then be calculated by applying principles of charge balance (see footnote *a* to Table I).

The procedure was validated by experiments in which a mixture of 0.2 mmol of $CuSO_4 \cdot 5H_2O$ with a known quantity of sodium

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(14) Use of an insufficiency of NH_3 allows any iodate that may be formed to react with iodide in an acidic medium. The presence of unreacted iodate in the citrate solution will lead to a drifting end point. In calculation of the amount of NH_3 required, allowance must be made for consumption of HBr during dissolution of the sample; specifically, each 1 mmol of sample consumes 2*y* mmol of HBr. Washing with 2 M KBr minimizes loss of bromine by volatility.

(15) If only very small quantities of Cu(III) are present (<5 μmol), better results are obtained by having the citrate present in the ammoniacal solution to which the sample is added. This prevents initial formation of CuI and avoids errors resulting from its incomplete redissolution.

(16) Amylose gives a somewhat sharper end point than ordinary soluble starch and permits estimation of the end point to about 0.2 μmol of thiosulfate. If greater sensitivity is needed, the end point can be determined potentiometrically (see, for example: Anderson, F. L.; Appelman, E. H. *Anal. Chem.* **1965**, *37*, 298).

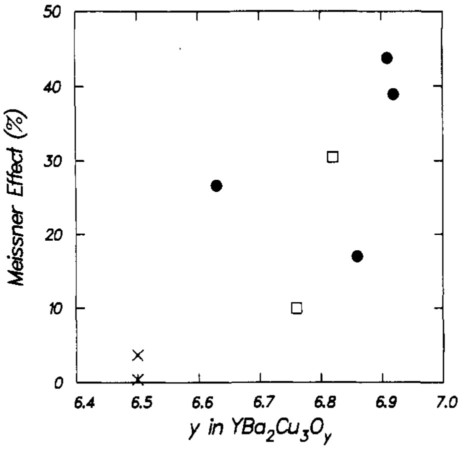

Figure 1. Percent Meissner effect (% M) vs oxygen content (y) for orthorhombic and tetragonal phases of $YBa_2Cu_3O_y$. Solid circles correspond to ceramic pellets, and open squares correspond to calcined powders, all of the orthorhombic phase. Crosses correspond to the quenched tetragonal phase.

bromate was substituted for the unknown oxide. In three validation experiments 1.664, 1.664, and 0.832 mg of sodium bromate were taken and 1.660, 1.660, and 0.829 mg were found.

Oxygen Content and Superconducting Properties. The results of analyses of five Cu–O materials by our Cu(III) iodometric method are summarized in Table I. Replicate analyses show excellent agreement. We estimate that the total uncertainty in the oxygen content y is ~±0.003 for a single determination on ~80 mg of $La_{2-x}Sr_xCuO_y$ or on ~40 mg of $YBa_2Cu_3O_y$. The oxygen content of the last sample given in Table I was determined also by H_2 reduction (to the assumed composition $YO_{1.5}$ + 2BaO + 3 Cu) with a Mettler TA-2 thermoanalyzer on 200-mg portions of the oxide heated to 900 °C. Duplicate analyses yielded y = 6.90 ± 0.03 and 6.92 ± 0.03, in excellent agreement with the more precise titration results. Among the drawbacks of the H_2 reduction method are its relatively poor precision, the uncertainty in reduction products, and serious errors resulting from discrepancies in metal ratios. For example, H_2 reduction of $YBa_2Cu_3O_{6.90}$ containing 5% CuO by weight would yield an apparent $y = 7.18$ whereas the Cu(III) titration of the same mixture would yield $y = 6.88$.

One observes that, in $La_{2-x}Sr_xCuO_y$, $y \simeq 4.00$ for both $x = 0$ and $x = 0.15$. Thus, the Cu(II):Cu(III) ratio is determined largely by the replacement of La(III) with Sr(II) without change in the oxygen content. Figure 1 illustrates a large range of measured oxygen contents for six different samples of orthorhombic $YBa_2Cu_3O_y$, plotted against the percent Meissner effect (% M). In these experiments, we obtained oxygen contents in the range $6.63 \leq y \leq 6.93$ for the orthorhombic phase. The lattice parameters of these materials (as either calcined powders or ceramic pellets) showed no correlation with oxygen content nor did they deviate significantly from the room-temperature lattice parameters reported from neutron diffraction measurements.[2] The average lattice parameters and standard deviations from the mean for the six samples reported here are a = 3.826 (3) Å, b = 3.892 (3) Å, and c = 11.678 (9) Å.

The Meissner effect was determined from the dc susceptibility measured at 30 K in a field of 53 Oe and was calculated from the ratio of the volume susceptibility without a demagnetization correction to that of a perfect superconductor ($\chi = -1/4\pi$). The Meissner effect is a convenient comparison for both the powdered samples of calcined product and the O_2-annealed ceramic pellets. Figure 1 suggests that % M generally increases with increasing oxygen content, but other factors such as defects and perhaps grain size may play a role. In any case, a reasonable extent of bulk superconductivity (% M ≥ 25) seems to occur for oxygen contents y between ~6.6 and 6.9. We observed no appreciable differences in the resistively measured superconducting transitions for the ceramic pellets: T_c(midpoint) = 88.3 K for $y = 6.63$ and 92.2 K for $y = 6.93$, with comparable 10–90% transition widths of ~2 K. One should note, however, that the resistive measurements may be sampling only a microscopic portion of the specimen, whereas the oxygen analyses and susceptibility measurements pertain to a macroscopic sample with perhaps inhomogeneous properties. Thus, for low values of y, high resistive T_c values could be the result of the filamentary contribution of material with higher oxygen content.

For comparison, we have included in Figure 1 the data for two tetragonal-phase samples of $YBa_2Cu_3O_y$. These samples are both analyzed as $y = 6.50$ [no Cu(III)], as expected on the basis of previous neutron diffraction studies of this high-temperature phase.[2] One sample (% M = 0.4) exhibited semiconductive resistive behavior, and the other (% M = 3.7) exhibited a broad superconducting transition beginning near ~60 K. The Meissner effects indicate the existence of very little bulk superconductivity, and again the resistive superconducting behavior could be due to microscopic amounts of the oxygen-rich orthorhombic phase.

In summary, we have developed and described in this communication a modified iodometric titration method that we believe to be an accurate and efficient procedure for measuring the Cu(III) content of Cu-containing superconducting oxides and, thus, the oxygen content. In applications of this method, we find that the room-temperature orthorhombic phase of $YBa_2Cu_3O_y$ can support a large variation in oxygen content y without change in lattice parameters or appreciable impairment of the resistive superconducting transition or diamagnetic properties.

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