done in the study reported here.

Si^+ (^2P) ions were found to react rapidly at 296 ± 2 K with several simple molecules containing hydroxyl groups. $SiOH^+$, conceivably formed by H-OH or C-OH bond insertion, was observed to be the predominant product ion with water, methanol, ethanol, formic acid, and acetic acid. Reactions of atomic silicon ions which produce $SiOH^+$ are of interest in molecular synthesis. For example, in interstellar and other ionized gaseous environments in which $SiOH^+$ may neutralize by electron/ion recombination or proton transfer, such reactions provide possible routes toward the formation of silicon monoxide.[8,9]

The chemistry of $SiOH^+$ was seen to have interesting consequences. An ion likely to be protonated silanoic acid was observed to be produced from $SiOH^+$ by addition with water and by dehydration with ethanol and formic acid. Neutral silanoic acid is a likely direct product of the reaction with acetic acid in which the acetyl ion was observed to be eliminated. The reactions with ethanol, formic acid, and acetic acid were observed to be rapid and bimolecular. A single mechanism involving O-H bond insertion of the $SiOH^+$ silene cation provides a plausible explanation for all of the results obtained with this ion.

Insertion appears to be a common mechanistic feature of the bimolecular reactions observed with Si^+ and $SiOH^+$. The overall energetics of the reactions with Si^+ constrain this ion to insert into the C-OH bond of the hydroxyl-containing molecules investigated. The energetics of the reactions of $SiOH^+$ are less well known but the predominant reaction features observed can be rationalized in terms of O-H bond insertion characteristic of analogous reactions of neutral carbenes.

With the molecules containing hydroxyl groups Si^+ initiates reaction sequences which appear to saturate the silicon center. With formic acid complete saturation appears to be achieved in three bimolecular steps as shown in reaction 14, or in four steps as shown in reaction 15. With acetic acid the silicon appears in the neutral product in the second step so that further saturation could not be followed in the experiment. With water, methanol, and ethanol the bimolecular reaction sequence stopped at $SiOH^+$ after one step, at $SiOCH_3{}^+$ after one or two steps, and at $SiOC_2H_5{}^+$ after two steps, respectively. With ethanol the experimental data were consistent with the additional bimolecular reaction sequences shown in 16 and 17. In some instances the

$$Si^+ \rightarrow SiOH^+ \rightarrow HSi(OH)_2{}^+ \rightarrow HSi(OH)_3H^+ \quad (14)$$

$$Si^+ \rightarrow SiOH^+ \rightarrow HSi(OH)_2{}^+ \rightarrow HSi(OCHO)OH^+ \rightarrow HSi(OCHO)(OH)_2H^+ \quad (15)$$

$$Si^+ \rightarrow SiOH^+ \rightarrow HSi(OH)_2{}^+ \rightarrow HSi(OH)_3H^+ \quad (16)$$

$$Si^+ \rightarrow SiOH^+ \rightarrow HSi(OH)_2{}^+ \rightarrow HSi(OC_2H_5)OH^+ \quad (17)$$

terminal ions of the bimolecular reaction sequences were observed to add further molecules of reactant in what are presumably termolecular association reactions. These may also lead to more saturated Si ions as, for example, in the reaction sequences 6 and 7 which may lead to $HSi(OCH_3)_3H^+$ and $HSi(OC_2H_5)_3H^+$, respectively.

The ion/molecule reaction sequences initiated by Si^+ investigated in this study increase the oxygen/silicon coordination number and so are of interest in molecular synthesis. For example we have seen how silicon monoxide and silanoic acid may be produced. Neutralization by proton transfer or recombination with electrons of the terminal ions in the reaction sequences 6, 7, and 15 may produce $HSi(OCH_3)_3$, $HSi(OC_2H_5)_3$, and $HSi(OCHO)(OH)_2$, respectively. Also, it is not difficult for the $HSi(OH)_3H^+$ produced as a terminal ion in the reaction sequences 14 and 16 to generate trihydroxysilane by neutralization. Subsequent hydride abstraction or reionization of this molecule followed by a dehydrative reaction between the unsaturated $Si(OH)_3{}^+$ fragment ion and carboxylic acid, in analogy with reaction 12b, may generate tetrahydroxysilane, $Si(OH)_4$, on neutralization. Tetrahydroxysilane is a building block for condensational synthesis of hydrated silicate networks.[21,22]

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The Influence of Oxygen Variation on the Crystal Structure and Phase Composition of the Superconductor $YBa_2Cu_3O_{7-x}$

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Abstract: On the basis of iodometric determinations of the oxidation state of Cu in $YBa_2Cu_3O_{7-x}$, TGA experiments, and equilibrium reactions, the highest oxygen content of 6.96 (2) is achieved when annealing in O_2 at about 440 °C. Annealing in air or oxygen in the range 350–450 °C produced material which analyzed as 6.94 (2). The orthorhombic phase exists over the composition range $O_{6.96}$–$O_{6.60}$. The tetragonal composition $YBa_2Cu_3O_6$ is prepared by heating the mixture in an inert atmosphere, Ar or N_2, at temperatures in excess of 700 °C. The oxygen solution range for this phase ranges from $O_{6.0}$ to $O_{6.15}$. Compositions with nominal oxygen contents of 6.15–6.60 may be mixtures of the tetragonal and orthorhombic phases.

The superconducting compounds with general formulas $Ln_{2-x}M_xCuO_{4-x}$ (M = Ba, Sr) and $LnBa_2Cu_3O_{7-x}$ display variations in oxygen content that strongly influence the superconducting property. During the investigation of the range of values of x in the latter stoichiometry we prepared single crystals of $YBa_2Cu_3O_6$ and determined its crystal structure.[1] This compound is tetragonal and is a semiconductor. The change of crystal system upon loss of oxygen may imply a limited range of oxygen solubility for each phase, and we carred out a systematic investigation of the vari-

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Table I. Preparative Conditions for $YBa_2Cu_3O_{7-x}$[a]

no.	temp (°C)	time (h)	atmosphere	condition	oxygen content (±0.02)	phase analysis X-ray diffraction
1	900	24	air	quenched	6.32	tetragonal + orthorhombic
2	900	24	air	cooled in the furnace	6.87	orthorhombic
3	690	12	O_2	cooled in the furnace	6.88	orthorhombic
4	690	12	50% O_2 + 50% Ar	cooled in the furnace	6.85	orthorhombic
5	510	6	air	quenched	6.79	orthorhombic
6	450	6	air	quenched	6.85	orthorhombic
7	440	24	O_2	cooled in the furnace	6.96	orthorhombic
8	440	24	50% O_2 + 50% Ar	cooled in the furnace	6.96	orthorhombic
9	350	72	air	cooled in the furnace	6.94	orthorhombic
10	350	9	O_2	cooled in the furnace	6.94	orthorhombic
11	590	7	Ar	cooled in the furnace	6.18	tetragonal + orthorhombic
12	600	20	Ar	cooled in the furnace	6.12	tetragonal
13	620	20	Ar	cooled in the furnace	6.12	tetragonal
14	450	16	N_2	quenched	6.64	orthorhombic
15	470	19	N_2	quenched	6.54	orthorhombic + tetragonal
16	800	20	N_2	quenched	5.99	tetragonal

[a] All oxygen compositions are from an iodometric determination of the valence of Cu.

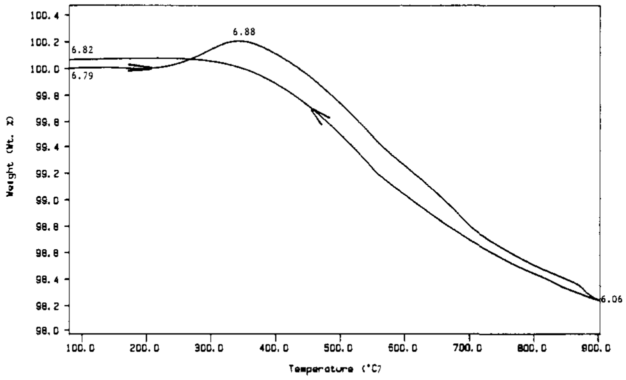

Figure 1. Heating and cooling in O_2 of specimen 5 at 1 deg/min. The numbers in this and subsequent thermogravimetric curves refer to oxygen composition.

ability of x in the phase $YBa_2Cu_3O_{7-x}$, $0 \le x \le 1$, using chemical, thermal, and X-ray diffraction techniques.

Experimental Section

$YBa_2Cu_3O_{7-x}$ was prepared by mixing Y_2O_3, $BaCO_3$, and CuO and firing at 950 °C in air as previously described in a phase diagram determination.[2] All products were examined by powder X-ray diffraction techniques using a Philips diffractometer fitted with a diffracted beam monochromator and Cu Kα radiation, and only those specimens were retained for further analysis that were single-phase as judged by this test. All starting materials as well as all materials subjected to annealing procedures and thermal analyses were also chemically analyzed by the iodometric determination of the oxidation state of Cu. The average oxidation state of Cu and hence the total oxygen content of the sample was determined by dissolving about 100 mg of sample in a solution consisting of 15 mL of 10% KI and about 5 mL of 3.5 N HCl. The solution was diluted with about 10 mL of distilled water, and the liberated I_2 was titrated with standardized sodium thiosulfate with starch as the end point indicator. All analyses were done in duplicate. The final oxygen stoichiometry has an error limit of ±0.02. The thermogravimetric analyses were carried out in a Perkin-Elmer Series 7 thermal analysis system in oxygen, nitrogen, and argon atmospheres.

Results

The compound that was prepared at 950 °C in air was single-phase orthorhombic and served as the starting material for 16 specimens that were subjected to various annealing conditions as shown in Table I. The oxygen content was determined by iodometric titration and the phases were identified by powder X-ray diffraction.

The TGA curve for sample 5 heated and cooled in an O_2 atmosphere at 1 deg/min is shown in Figure 1. No weight change occurs to 220 °C; thereafter O_2 diffuses into the crystal structure until a balance between O_2 gain and loss is reached at 350 °C, producing a composition containing $O_{6.88}$. Subsequent heating produces a continuous weight loss until at 905 °C the composition is $YBa_2Cu_3O_{6.06}$. The end point of the cooling cycle corresponds to $YBa_2Cu_3O_{6.82}$. The X-ray powder diffraction pattern showed that this product was single-phase orthorhombic.

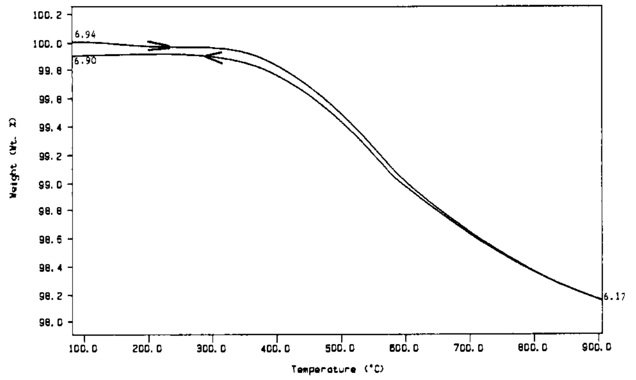

Figure 2. Heating and cooling of specimen 10 in O_2 at 2 deg/min.

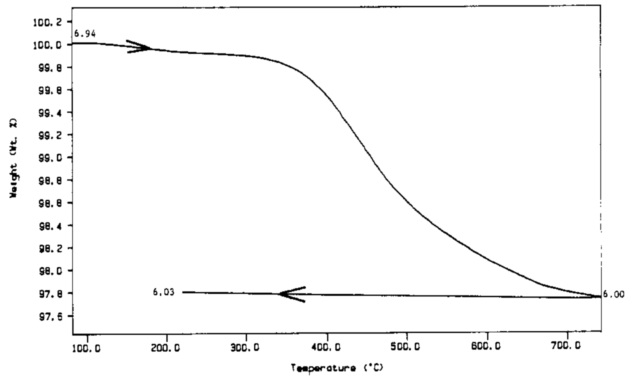

Figure 3. Heating of specimen 10 in N_2 at 2 deg/min and cooling in the same atmosphere at 20 deg/min.

The X-ray diffraction pattern obtained from specimen 10 showed it to be single-phase, orthorhombic material. Heating and cooling in O_2 at 2 deg/min (Figure 2) produced the composition $O_{6.17}$ at 905 °C, and during the cooling cycle to room temperature O_2 had reversibly diffused into the structure to yield $O_{6.90}$. This product was single-phase orthorhombic. The onset of loss of O_2 occurred at about 350 °C. A change of slope, $\Delta W/\Delta T$, occurs near 600 °C, corresponding to the approximate composition $O_{6.5}$. Specimen 10 was also heated in N_2 at 2 deg/min, (Figure 3). Rapid loss of O_2 begins at 360 °C and at about 745 °C reaches the composition $O_{6.0}$. Cooling at 20 deg/min in N_2 to 220 °C essentially maintains the 6.0 composition. There is an indication

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[2] Steinfink, H.; Swinnea, J. S.; Sui, Z. T.; Hsu, H. M.; Goodenough, J. B. *J. Am. Chem. Soc.* **1987**, *109*, 3348.

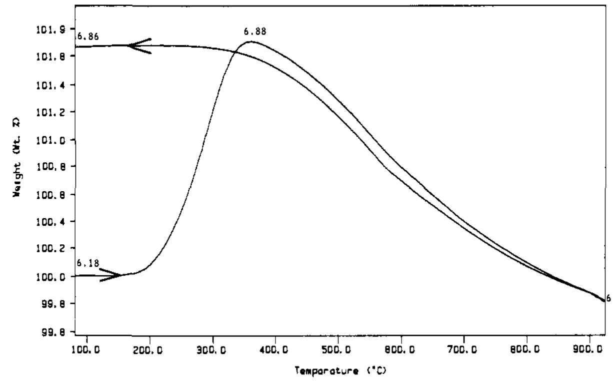

Figure 4. Heating and cooling of specimen 11 in O_2 at 1 deg/min.

of slight O_2 uptake probably from O_2 contamination of the N_2. The X-ray diffraction pattern obtained from this end product was single-phase tetragonal. An inflection point at 480 °C on heating corresponds to the composition $O_{6.42}$.

Specimen 11 was subjected to a TGA run in which it was heated and cooled in flowing O_2 at 1 deg/min (Figure 4). Initial O_2 uptake begins at about 180 °C and accelerates rapidly between this temperature and 360 °C at which the composition is $O_{6.88}$, a value that represents a balance between uptake and loss of O_2. At increasing temperatures O_2 is lost and the oxygen composition 6.11 is reached at 925 °C. Cooling to room temperature produces a material with $O_{6.86}$. This product is single-phase orthorhombic. An inflection point in the curve near 600 °C corresponds to $O_{6.5}$.

Sample 9 was heated to 985 °C and cooled to room temperature in O_2 at 1 deg/min in the TGA apparatus. At the end of the run the composition of the orthorhombic phase had returned to $O_{6.94}$ after reaching $O_{6.07}$ at 985 °C. However, on the cooling cycle O_2 uptake between 985 and 900 °C was rapid and then assumed normal behavior below 900 °C. The discontinuity corresponded to the composition $O_{6.26}$. The powder X-ray diffraction pattern of the product at room temperature showed that some decomposition to Y_2BaCuO_5 had occurred.

The powder X-ray diffraction patterns of several preparations in which O_2 had been chemically determined appeared to show the presence of both the orthorhombic and tetragonal phases. The inflection points in the TGA curves were seen near oxygen compositions of 6.5 and were considered to be possibly due to a phase change at that temperature from the orthorhombic to the tetragonal phase. In order to delineate the phase boundaries precisely specimens were prepared with varying oxygen contents that were determined iodometrically and then investigated by powder X-ray diffraction. This technique was thought to be particularly sensitive for this determination because of the intensity relationships of two sets of lines: (a) the 013, 103 + 110 lines of the orthorhombic phase and the 103, 110 lines of the tetragonal phase ($31.5° < 2\theta < 33.5°$ for CuK_α); (b) the 006 + 020, 200 lines of the orthorhombic phase and the 006, 020 for the tetragonal phase ($45° < 2\theta < 47°$).[1,2]

From Table I it is seen that specimen 14 was single-phase orthorhombic, while 15 could be interpreted to contain both phases, suggesting a lower limit of the oxygen deficiency for the orthorhombic phase to be $YBa_2Cu_3O_{6.60(5)}$. Specimens 11 and 12 appeared to bracket the upper limit of the oxygen content of the tetragonal phase to which we assign the composition $YBa_2Cu_3O_{6.12(3)}$. This limit is chosen because the $O_{6.18}$ specimen could be interpreted as having an orthorhombic component while $O_{6.12}$ did not show any presence of that phase.

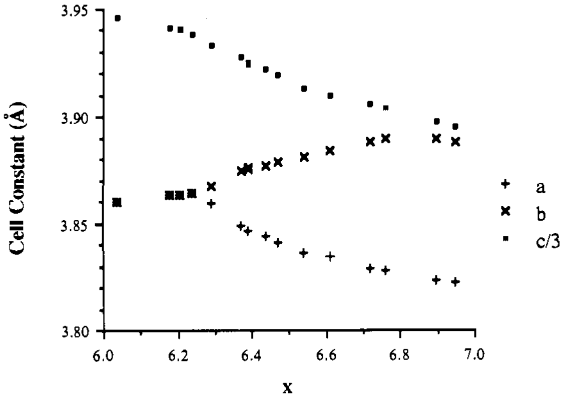

Figure 5. Lattice constants versus oxygen content in $YBa_2Cu_3O_x$.

Note Added in Proof: In Figure 5 are shown the changes of the lattice parameters with composition for $YBa_2Cu_3O_x$. Sixteen samples were prepared by heating between 400 and 800 °C for 24 h in N_2 and quenched to room temperature in N_2; the oxygen compositions were determined by Rietveldt analyses of the powder X-ray diffraction patterns. The diffraction lines had a fwhm of about 0.14°, and the estimated standard deviations for a and b are ±0.00011 Å and for c it is ±0.0004 Å. A smooth orthorhombic to tetragonal transition is observed near $O_{6.27}$. This represents an alternate interpretation of the X-ray data. A change of slope of the $^1/_3c$ parameter occurs near $O_{6.55}$.

Discussion

We made numerous attempts to prepare material that would yield an $O_{7.00}$ composition on the basis of the iodometric determination. The highest value that we achieved by annealing in flowing O_2 at 440 °C for 24 h was 6.96. The X-ray powder diffraction pattern showed very well crystallized, single-phase, orthorhombic material. This stoichiometry may represent the maximum equilibrium value for an O_2 partial pressure of 1 atm. The thermogravimetric analyses show that the initial loss of O_2 occurs fairly rapidly but a marked change in the slope occurs at a composition near $YBa_2Cu_3O_{6.5}$. At this composition all of the Cu is divalent and this material may no longer be superconducting. The loss of superconductivity could possibly occur at a higher oxygen value. A point may be reached where the large number of oxygen vacancies destroys the continuity of the CuO_3 chains even though the orthorhombic structure is still retained.

A study of T_c as a function of x for $YBa_2Cu_3O_{7-x}$[3] shows T_c of 90 K for a sample with nominal compositions of 6.8 and 55 K for a sample with nominal composition 6.6. Samples with compositions 6.5 and 6.4 show behaviour due to the presence of two (or more) phases. The compositions reported in that paper were based solely on TGA data.

The slight decomposition of a specimen heated in O_2 to 985 °C indicates that a safe upper limit for preparation of the orthorhombic phase is <985 °C.

Acknowledgment. This research was supported by National Science Foundation Grant DMR8520028 and by the R. A. Welch Foundation, Houston, Texas.

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(3) Tarascon, J. M.; McKinnon, W. R.; Greene, L. H.; Hull, G. W.; Bagley, B. G.; Vogel, E. M.; LePage Y. Proceedings of the Symposium "High Temperature Superconductors with T_c over 30 K"; Materials Research Society, 1987; in press.