JOURNAL OF SOLID STATE CHEMISTRY **92**, 327–338 (1991)

Determination of the Oxygen Content in Superconducting and Related Cuprates Using Temperature-Programmed Reduction

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Received July 26, 1990; in revised form January 21, 1991

The oxygen content and reducibilities of four base metal oxides, six nonconducting cuprates, and three superconducting cuprates were investigated by temperature-programmed reduction (TPR) from 30 to 900°C. It was shown that the copper, bismuth, and thallium ions of these oxides were reduced to the zero valence state. Thus, TPR is a useful technique for determining the actual oxygen stoichiometry of cuprates. For multiphase $Bi_2CaSr_2Cu_2O_{8+x}$ and $Tl_2CaBa_2Cu_2O_{8+x}$ superconductors pretreated in air, x was found to be 2 ± 0.2 and 1 ± 0.2, respectively. Both values are significantly higher than previously reported. The reduction of superconducting and related cuprates required higher temperatures than CuO, but the reducibility of CuO decreased when it was calcined in air at 940°C. The Bi- and Y-based superconducting cuprates exhibited the lowest reducibility among the samples investigated. © 1991 Academic Press, Inc.

Introduction

Temperature-programmed reduction (TPR) is a convenient and rapid technique to determine the oxygen content and reducibility of metal oxides, provided their reduction is thermodynamically feasible (*1, 2*). The technique is frequently used to characterize supported and unsupported cupric oxide (*1–5*) or copper-exchanged zeolite (*1, 2, 6–9*) catalysts. Recently, superconducting and related cuprates have attracted increasing attention as a new group of copper containing catalysts (*10–17*). Regarding CO oxidation (*17–20*), the activities of these cuprates were found to be strongly dependent on the extent of surface reduction. Therefore, a knowledge of their reducibilities is desirable for better understanding of their catalytic behaviors.

TPR experiments provide a new means to determine the actual oxygen content of superconducting oxides. This knowledge may contribute to an understanding of why the transition temperature, T_c, can be changed dramatically by varying the conditions of oxygen treatment (*21–25*). There are many apparent contradictions in the interpretations of the oxygen effect, which can be attributed to uncertainties in the oxygen content of the more complicated superconducting cuprates.

For example, the T_c of yttrium (*26–30*)-,

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0022-4596/91 $3.00

bismuth (*31–33*)-, and thallium (*34–38*)-based superconductors ranges from 0 (nonsuperconducting) to 92, 110, and 132 K, respectively, depending on the oxygen partial pressure, annealing temperature, cooling rate, etc. For $YBa_2Cu_3O_{6.5+x}$, it is generally accepted that T_c decreases with decreasing x (*21, 22, 26*). In contrast, T_c was observed to increase (*32, 33, 37, 39*) when the oxygen content decreased in several Bi and Tl superconductors. However, both behaviors in which T_c passes through a maximum (*24, 31, 36*) and T_c is constant (*36, 40*) as a function of oxygen content have also been reported.

Numerous methods have been used to determine the oxygen content of $YBa_2Cu_3O_{6.5+x}$. The lattice constants and ion positions of tetragonal $YBa_2Cu_3O_{6.5}$ and orthorhombic $YBa_2Cu_3O_7$ phases were identified by single crystal X-ray and neutron and electron diffraction (*22, 41–43*). Determination of oxygen content by the thermogravimetric technique (*18, 43–45*) requires the assumption of a single phase being present. For example, superconductors with a starting nominal composition of $YBa_2Cu_3O_{6.5+x}$ were assumed to be fully oxidized to $YBa_2Cu_3O_7$ by repeated heat treatment in a stream of oxygen. The value of x can then be calculated from the weight uptake. The powder X-ray diffraction method (*21, 22, 26–29*) is based on the correlation between the oxygen content and cell volume contraction, assuming a gradual change from $YBa_2Cu_3O_7$ to $YBa_2Cu_3O_6$. The volumetric method of Conder *et al.* (*46*) is reported to have the best (±0.001) accuracy in determining x. They measured the volume of oxygen evolved from the reaction of Cu^{3+} with H_2O, after dissolving a sample of $YBa_2Cu_3O_{6.5+x}$ in diluted acid. A similar solution is used for determining the average copper valence by iodometric titration (*45–50*). This method has also been widely used for determining the oxygen content of Y–Ba–Cu–O superconductors, assuming that the oxygen treatment affects only the oxidation state of copper. By directly measuring the oxygen content using hydrogen reduction and gravimetric techniques, deLeeuw *et al.* (*48*) found that yttrium and barium cuprates produced Y_2O_3, BaO, and Cu when they were heated at 900°C in hydrogen. The measured weight loss, corrected for other desorbing impurities such as H_2O and CO_2, was used to calculate the original oxygen content.

All these methods showed that x in $YBa_2Cu_3O_{6.5+x}$ may vary between -0.5 and $+0.5$. The oxidation is usually described as progressive incorporation of divalent oxygen into the oxygen-deficient sites of the perovskite lattice, accompanied by a corresponding increase of the formal charge of copper (*21, 22, 27–29, 49, 50*). Instabilities in the resulting superlattice structure, as well as mixed valence states, are widely used to explain the superconductivity observed in these oxides (*21, 50*). However, the interpretation of the effect of oxygen has recently become more complicated. XPS (*51–54*), XAES (*53*), XANES (*54, 55*), and other investigations (*51*) have indicated the absence of Cu^{3+} ions and the presence of peroxide O^- ions in the yttrium superconductors.

In contrast to $YBa_2Cu_3O_{6.5+x}$, the oxygen content of bismuth and thallium superconductors are not well characterized. The idealized tetragonal structures of numerous compounds of the type $A_mM_2Ca_{n-1}O_{2n+m+2}$ (*21, 56*), where A can be Tl, Bi, Pb, or a mixture of them and M represents Ba or Sr, have been identified by single crystal X-ray, neutron, and electron diffraction (*21, 56*). Their oxygen content is calculated based on the assumption of the presence of Tl^{3+}, Bi^{3+}, Pb^{2+}, Cu^{2+}, and O^{2-} ions in addition to 2+ alkali earth ions (e.g., $Bi_2CaSr_2Cu_2O_8$, $Tl_2Ca_2Ba_2Cu_3O_{10}$). Nevertheless, the possibilities of variable valence states of copper and oxygen are similar to the yttrium-based superconductors, and Tl^+, Pb^{4+}, and Bi^{5+} valences have also been indicated by several analytical methods (*21, 50, 59–63*). In addition, the presence of an idealized lattice structure is not enough to determine the oxygen stoichiometry, even for a material of a single phase. This is because the crystal structures are incommensurate. Moreover, the cations can substitute for each other on lattice positions having different oxygen coordinations, and cation deficiencies were frequently observed (*21, 33, 39, 57, 63*). It should be noted that the majority of samples used for electrical resistance and magnetic measurements are multiphasic, with the possible presence of innumerable intermediate compounds, nonreacted starting materials, and other superconducting homologs (*31–39, 58*). The possible existence of oxygen-deficient sites in the perovskite-type structure and the localization of excess oxygen within the BiO and TlO layers (*21, 31, 33, 39, 64–66*) enable further variations in oxygen content. The possibility for intercalation of excess oxygen between the double BiO and TlO layers has also been suggested (*36, 66, 67*).

These peculiarities of bismuth and thallium cuprates suggest that their oxygen content can significantly differ from the $A_mM_2Ca_{n-1}Cu_nO_{2n+m+2}$ average compositions, and thus it is important to gain a knowledge of their current oxygen content. However, among the methods used to determine the oxygen content of $YBa_2Cu_3O_{6.5+x}$, only the gravimetric procedure of deLeeuw *et al.* (*48*) is reliable. It measures the absolute oxygen content of the actual superconducting compositions, regardless of the number and type of phases or impurities. The technique does not require the assumption of an oxygen stoichiometry or the oxidation state of ions, provided that all reducible ions are reduced to the zero valence state in H_2 at 900°C. Despite the very large body of literature concerning the effect of oxygen on bismuth and thallium superconductors, there are only a few papers (*33, 65, 66, 68*) in which the oxygen content was determined by the gravimetric procedure. All these papers reported surplus oxygen for samples of the type $Bi_2(CaSr)_3Cu_2O_{8+x}$. The value of x was found to be around 0.2 to 0.3. The excess oxygen was also confirmed by chemical titration methods, which assume that copper is the only ion undergoing redox. However, in some cases (*65, 66*) the oxygen contents determined by TGA were found to be about 60% higher than those obtained by chemical titration. This indicates that copper ions are probably not the only species which determine the oxygen content. It is also interesting that the value of x was reported to be around $+0.3$ for a sample of $Bi_2Sr_2Ca_{0.9}Y_{0.1}Cu_2O_{8+x}$, even after annealing it at 10^{-4} bar oxygen partial pressure at 600°C (*33*). This result indicates that the oxygen content of a well-oxidized, carefully cooled sample is probably much higher. Similar findings were implicit in the results for $TlBa_2CaCu_2O_7$ (*21*) and $(Tl_{1-x}Bi_x)Sr_2Ca_2Cu_3O_9$ (*56*), which contain more O^{2-} than the theoretical amount based on Bi^{3+}, Tl^{3+}, and Cu^{2+}. However, the "excess" oxygen was not discussed. Our TPR experiments provide evidence for the possibility of a higher oxygen content in these families of superconductors.

The determination of oxygen by TPR involves heating the samples in a stream of H_2, which is similar to the method of deLeeuw *et al.* (*33*). Nevertheless, it has the advantage that the hydrogen consumption provides direct measurements of reacted oxygen, and there is no need for additional determination of the possible desorption of H_2O, CO_2, or other impurities. This technique also shows the entire reduction process as a function of temperature. This paper discusses the determination of oxygen content by TPR for yttrium, bismuth, and thallium superconductors. TPR investigations of the most frequent nonsuperconducting impurities are also reported.

Experimental

Preparation and Characterization of Samples

Cuprates were prepared from well ground solid oxides, nitrates, or carbonates, followed by calcination in a porcelain crucible in air. The starting materials used were: Y_2O_3 (99.9%) and $Ba(NO_3)_2 \cdot 2H_2O$ (99.9%) from Merck Co., A.C.S. reagent grade CuO (99%) from Spectrum Chemical Mfg. Co., BaO (99%) from E.M. Science Industries, Inc., and Bi_2O_3 (99%), CaO (99.95%), SrO (99.99%), and Tl_2O_3 (99.999%) from Johnson and Matthey, Inc.

The preparation procedures for $BaCuO_2$ (*20, 69*), $Ba_2Cu_3O_5$ (*69, 70*), Y_2BaCuO_5 (*19, 69*), and $YBa_2Cu_3O_{6.5+x}$ (*14, 69, 71*) have been reported elsewhere. CuO(940) is prepared by calcining CuO in air at 940°C for 5 hr.

$Y_2Cu_2O_5$, Ca_2CuO_3, and Ba_2CuO_3 were synthesized from Y_2O_3, CaO, BaO, and CuO by mixing and calcining in air the corresponding stoichiometric mixtures of metal oxides at 940°C for a total of 20 hr. After the first 10 hr the products were cooled rapidly (400°C/hr) to room temperature and reground. The cooling rate after the second 10-hr period of heating was about 150°C/hr.

The $Bi_2CaSr_2Cu_2O_8$ superconductor was prepared from Bi_2O_3, CaO, $SrCO_3$, and CuO with 1:2:2:4 mole ratios, respectively. The starting mixture was heated at 880°C for 8 hr, then cooled at a rate of 50°C/hr.

For the preparation of the $Tl_2CaBa_2Cu_2O_8$ superconductor, stoichiometric amounts of Tl_2O_3, $BaCuO_2$, and CaO were heated at 920°C for 10 min. The cooling rate was 50°C/hr.

The phase compositions of the samples were investigated using a Rigaku Model CN4148H2 X-ray diffractometer equipped with a 12-kW rotating anode. The X-ray powder patterns were analyzed using the computerized JCPDF data base and data from Refs. (*70*) and (*72–75*).

The magnetic susceptibilities of the superconducting samples of $YBa_2Cu_3O_{6.5+x}$, $Bi_2Ca_2Sr_2Cu_4O_x$, and $Tl_2CaBa_2Cu_2O_{8+x}$ were measured using a Quantum Desire magnetometer. Critical transition temperatures of 90, 86, and 112 K were observed for the Y, Bi, and Tl samples, respectively.

TPR Apparatus and Procedures

The reducing gas for all TPR experiments was a mixture of 94.5 vol% high purity (99.999%) argon and 5.5 vol% of hydrogen (99.99%). Details of the TPR system have been described previously (*76*). For a typical TPR experiment, 5–60 mg of sample were loaded in a quartz reactor (i.d. 5 mm) of the flow-through type. After connecting the reactor, the whole TPR system, including tubing, gas manifold, and Gow-Mac Model 10-952 thermal conductivity detector (TCD), was evacuated to 1×10^{-6} Torr at 23°C. The evacuated system was then filled with the reducing gas. The reducing gas was first passed through the reference arm of the TCD before entering the reactor. The reactor's exit stream was directed through a trap at 195 K (to remove product water, etc.), thence to the second arm of the TCD, and finally to a flow meter. The flow rate was 20 ml/min at 101 kPa. The temperature of the reactor was linearly raised by an Omega Model CN8600 process controller at a rate of 15°C/min up to 900°C. The TCD output (H_2 consumption) was recorded on a strip chart recorder. The amount of H_2 reacted was calculated by comparison to calibration pulses containing known volumes of hydrogen. The hydrogen consumption of an empty reactor was found to be <0.01 ml.

TABLE I

OXYGEN CONTENT OF SUPERCONDUCTING AND RELATED CUPRATES DETERMINED USING TPR

			Hydrogen consumption [mL,STP]				
Sample no.	Oxide	Surface area (m^2/g)	Expected if $x = 0$	Measured	R	R_{av}	$x \pm \Delta x$
1.a	CuO_{1+x}	2.43	6.49	6.75	1.04	1.03	0.03 ± 0.04
1.b			1.42	1.43	1.01		
2.a	$CuO(940)_{1+x}$	0.29	7.56	8.25	1.09	1.09	0.09 ± 0.04
2.b			1.41	1.53	1.09		
3.	Tl_2O_{3+x}	nm	0.90	0.91	1.01	1.01	0.03 ± 0.27
4.	Bi_2O_{3+x}	nm	1.40	1.23	0.88	0.88	−0.36 ± 0.21
5.	Ba_2CuO_{3+x}	0.10	0.42	0.70	1.67	1.67	0.67 ± 0.17
6.	$BaCuO_{2+x}$	0.25	0.50	0.45	0.90	0.90	−0.10 ± 0.09
7.	$Ba_2Cu_3O_{5+x}$	0.54	0.68	0.64	0.94	0.94	−0.18 ± 0.28
8.	Ca_2CuO_{3+x}	nm	0.91	0.99	1.09	1.09	0.09 ± 0.10
9.	$Y_2Cu_2O_{5+x}$	0.29	0.74	0.79	1.07	1.07	0.14 ± 0.20
10.	Y_2BaCuO_{5+x}	0.48	0.48	0.49	1.02	1.02	0.02 ± 0.10
11.a	$YBa_2Cu_3O_{6.5+x}$	0.10	2.21	2.62	1.19	1.14	0.42 ± 0.14
11.b			0.49	0.51	1.04		
12.	$YBa_2Cu_3O_{7+x}$						−0.06 ± 0.14
13.a	$Tl_2CaBa_2Cu_2O_{8+x}$	0.69	7.04	8.25	1.17	1.13	0.65 ± 0.23
13.b			0.74	0.78	1.05		
14.	$Tl_2CaBa_2Cu_2O_{9+x}$						−0.24 ± 0.23
15.a	$Bi_2Ca_2Sr_2Cu_4O_{11+x}$	0.73	8.25	11.25	1.36	1.27	1.89 ± 0.18
15.b			1.07	1.38	1.29		
15.c			4.77	5.39	1.13		
15.d			1.25	1.54	1.23		
15.e			7.21	9.56	1.33		
16.	$Bi_2CaSr_2Cu_2O_{10+x}$						0.14 ± 0.18

Note. nm, not measured; R, measured/expected; R_{av}, average of R.

Results and Discussion

Table I summarizes the results of the oxygen content determination for different oxides by TPR. Figures 1, 2, and 3 show the TPR profiles of mono-, bi-, and multimetallic oxides, respectively. The XRD patterns showed that the majority of the cuprates investigated were practically single phase materials. However, the bismuth compound (sample 15 of Table I) contained Ca_2CuO_{3+x}, CuO, and traces (about 5%) of other unidentified impurities, besides about 70% of $Bi_2CaSr_2Cu_2O_{8+x}$ which is the source of the superconductivity. Small amounts (about 10%) of unreacted $BaCuO_2$ and CuO were also found in the thallium superconductor, containing $Tl_2CaBa_2Cu_2O_{8+x}$ as the major phase. The high baseline signals and low diffraction peak intensities on some diffraction patterns indicated that a part of these products was microcrystalline or amorphous. For example, the Ba_2CuO_3 sample was estimated to contain at least 50% of an amorphous phase.

An analysis of both systematic and random errors in determining the amount of H_2 consumption during TPR indicates that the error of a single measurement varies from about 5% for a sample consuming ≥ 5 ml of H_2 to 9% for a sample consuming 0.5 ml of H_2. In some cases additional samples were analyzed to improve the accuracy by averaging the results.

The expected amount of H_2 consumption is readily calculated from the weight of a sample and the assumption that the elements Cu, Tl, and Bi are initially present as Cu^{2+}, Tl^{3+}, and Bi^{3+}, and that they are all reduced to the zero valent state during TPR. This corresponds to the value of x given in the formulas of column two being zero. The expected amount of H_2 consumption is given by the formula

$$\text{amount (ml,STP)} = 22{,}400(g/F)(n_{Cu} + 1.5n_{Tl} + 1.5n_{Bi}),$$

where g is the mass of the sample in grams, F is the gram formula weight of the sample, and n_i is the number of ions of type i per formula unit. The sixth column of Table I gives the value R, defined as the ratio of the measured to expected amount of H_2 consumption. The seventh column gives the average value of R, R_{av}, which is weighted according to the accuracy of each measurement. Most of the compounds and especially all of the superconductors have $R_{av} > 1$, indicating the presence of excess oxygen. The amount of excess oxygen per mole of compound, x, is given by the formula

$$x = (R_{av} - 1)(n_{Cu} + 1.5n_{Tl} + 1.5n_{Bi}),$$

and is shown in column eight. Error in the value of x, Δx, is due to the error in R_{av}, and is relatively large since x is the difference between two numbers of similar size. Since each of the superconducting samples (numbers 11, 13, and 15) had substantial excess oxygen, the results were recalculated using the stoichiometry shown as samples 12, 14, and 16. Samples 12 and 14 can be interpreted as having either one Cu^{3+} or one O^- per formula unit, and sample 16 can be interpreted as having Bi^{5+}.

Base Metal Oxides

CuO and Tl_2O_3 were found to be totally reduced to metallic Cu and Tl. The TPR curve for Bi_2O_3 did not return to the base line up to 900°C (Fig. 1). This result indicates that the reduction is incomplete, which is reflected in a value of -0.36 for x in Table I.

Special care was taken in comparing the oxygen content and reducibility of CuO and CuO(940), because these oxides showed remarkable differences in catalytic activity for CO oxidation (*20*). A possible explanation for this behavior could be their different ease of partial reduction. As seen in Table I, their oxidation states were essentially the same. The very slight excess oxygen in CuO(940) is similar to that observed by Milliken and Cordaro (*77*) for oxygen-treated cupric oxides. A significant difference was obtained, however, in the temperatures for maximum hydrogen uptake (Fig. 1). The more difficult reducibility of CuO(940) is in good accordance with its higher light-off temperature observed in catalytic CO oxidation (*20*). As the X-ray powder patterns (*20*) and oxidation state of copper (Table I) for CuO and CuO(940) are practically identical, their different reducibilities can probably be attributed to their different morphologies (*77*) and the lower surface area of CuO(940).

In general, a single peak in TPR profiles has been observed for unsupported CuO (*1, 2, 4, 5, 78*) and the $Cu^{2+} \rightarrow Cu^0$ reduction is supposed to take part in one step without formation of Cu_2O (*79*). Our experiments (Fig. 1) suggest a reduction mechanism involving two steps. Similar resolutions were observed for supported CuO (*4*), or for Cu^{2+} exchanged zeolites (*1, 7, 8*), which were considered to demonstrate a gradual $Cu^{2+} \rightarrow Cu^+ \rightarrow Cu^0$ transition (*1, 2, 7*). Gentry *et al.* (*9*) have shown that by increas-

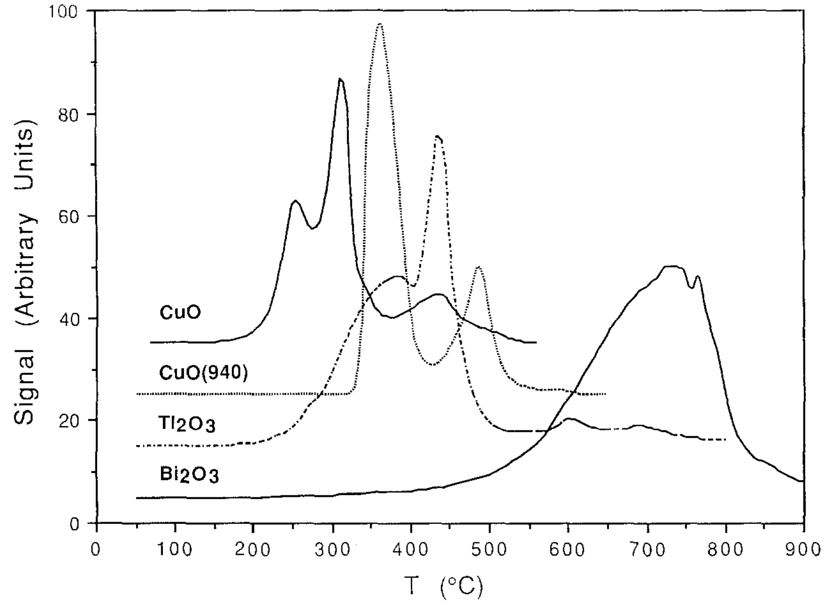

FIG. 1. TPR of base metal oxides.

ing the weight of samples the resolution of the two peaks disappears. Figure 1 shows TPR profiles for about 5 mg of CuO and CuO(940), which is 5 to 100 times less than has been used in other experiments. Using 20–25 mg from the same samples, the resolution of the peaks practically disappeared and the maxima of hydrogen uptakes for CuO and CuO(940) were at 320 and 425°C, respectively (not shown). The lower temperature corresponds to the range usually observed for CuO (*1, 2*). The decreased reducibility of CuO(940) indicates that not only the origin of copper oxide may influence the reducibility, as was observed previously (*1–3, 5*), but also the temperature of preparation.

Nonconducting Cuprates

As shown in Table I, the expected and measured oxygen contents are identical within the accuracy limits for all nonconducting cuprates (samples 5–10) except for Ba_2CuO_{3+x} (sample 5). These observations indicate that, in agreement with ESR results (*80*), the formal oxidation state of copper is 2+ in these compounds. The excellent agreement between the expected and measured oxygen contents validates the TPR technique for accurate determination of the oxygen stoichiometry of cuprates. The value of $x \cong 0.7$ obtained for Ba_2CuO_{3+x} suggest that Cu^{3+} or O^- ions are probably present in this oxide. The high oxygen content agrees with the expected behavior of the oxygen-deficient perovskite structure of $Ba_2CuO_{3.3}$ reported by de Leeuw *et al.* (*48*).

The reduction of copper was more difficult in all the cuprates investigated (Fig. 2) than in CuO (Fig. 1). The practically one-step reduction of yttrium and calcium cuprates takes place in a relatively narrow temperature range, while the TPR profile of barium cuprates is broad.

The two distinct peaks of the electrically insulating Y_2BaCuO_5 (Fig. 3) indicate that its reduction takes place in two steps. The

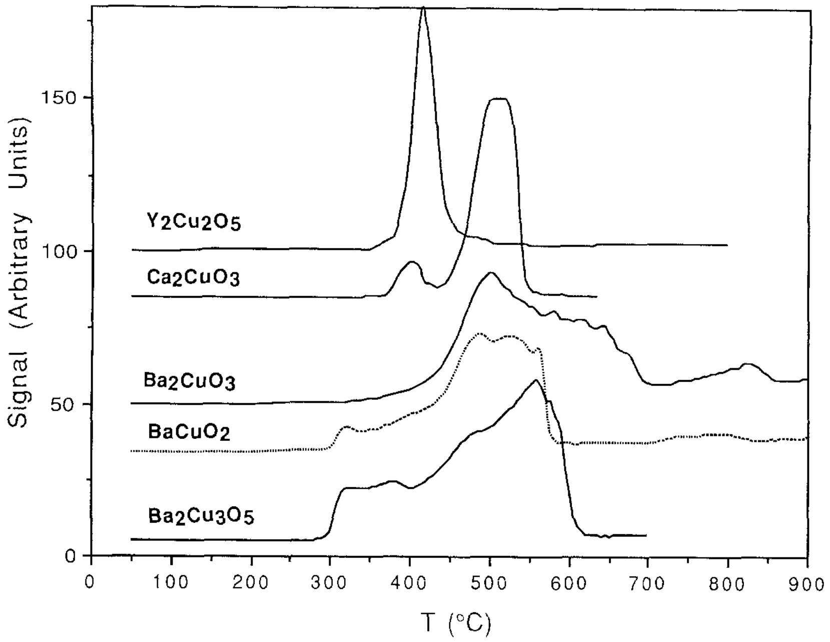

FIG. 2. TPR of bimetallic cuprates.

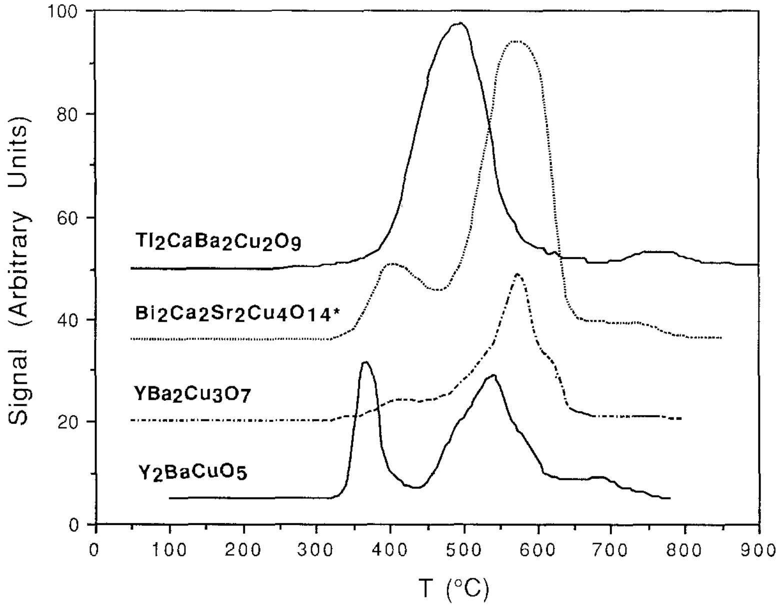

FIG. 3. TPR of multimetallic cuprates. *Nominal composition.

temperatures of maximum hydrogen uptakes and the shapes of the TPR peaks for this oxide are similar to those of the bimetallic yttrium and barium cuprates (Fig. 2). Besides the possibility of the distinct reduction steps of Cu^{2+} to Cu^{+} and Cu^{+} to Cu^{0}, a temporary formation of these compounds may also explain the two steps in decomposition of Y_2BaCuO_5.

Superconductors

The reduction process of the superconducting cuprates is shown in Fig. 3. The temperatures of maximum hydrogen uptake of the Bi- and Y-based samples are similar to each other, and they are the highest among the cuprates investigated. This harder reducibility correlates with their lowest catalytic activity among the cuprates (*17–20*). It is interesting to note that, unlike Bi_2O_3 (Fig. 1), the bismuth was completely reduced in the bismuth superconductor. The reduction of bismuth is probably facilitated by the presence of the reduced Cu, similar to the effects of copper on reduction of nickel in Ni–Cu alloy or palladium on reduction of Cu in Pd-doped CuO, etc. (*1*). A similar facilitating effect of Tl on reduction of copper may exist in the Tl-superconducting compound, which may be why it has the lowest decomposition temperature among the superconducting samples. A bump at around 320–420°C in the TPR curve of $YBa_2Cu_3O_{6.5+x}$ is characteristic of the well known nonstoichiometric oxygen (*21*) in the structure.

Particularly interesting are the measurements of the oxygen content of the superconducting samples. The value of $x = 0.42$ oxygen/mole, obtained for $YBa_2Cu_3O_{6.5+x}$ (sample 11 in Table I), agrees very well with the composition of $YBa_2Cu_3O_7$ (*22, 41–43*) (sample 12) for this type of superconductor. Approximately 6.9 oxygen was estimated for the same compound from our thermal gravimetric analysis (TGA) and XRD measurements.

For the Tl-based superconductor, $Tl_2CaBa_2Cu_2O_{8+x}$, the value of $x = 0.65$ suggests "excess" oxygen (sample 13 in Table I). Since the TPR results for $BaCuO_2$, CuO, and Tl_2O_3 showed the absence of surplus oxygen, the "excess" oxygen is not due to these impurities and is due to the superconducting phase. As shown in Table I (sample 14), the agreement between the expected and the measured hydrogen uptake is excellent if the stoichiometry $Tl_2CaBa_2Cu_2O_9$ is assumed. This result suggests that, similar to $YBa_2Cu_3O_7$, either Cu^{3+} or O^{-} ions are present in the Tl superconductor. However, observation of trapped O_2 has also been reported for both superconductors (*81–83*). The TPR results do not enable us to distinguish between structural, chemisorbed, and physisorbed oxygen. TGA measurements of the Bi- and Y-based superconducting oxides showed (*84*) a weight loss of about 0.2% when heated in a N_2 stream between room temperature and 400°C. Therefore the trapped O_2, if it exists, is less than 0.1 mole oxygen/mole oxide. No weight loss was observed for the Tl-based superconductor below 600°C.

Similar to the other two superconductors, a significant amount of "excess" oxygen was measured for the superconducting sample with nominal composition $Bi_2Ca_2Sr_2Cu_4O_{11+x}$ (Table I, sample 15). Supposing that the oxidation state of copper in Ca_2CuO_3 and CuO impurities is 2+, the expected and measured hydrogen uptake agrees very well with the composition $Bi_2CaSr_2Cu_2O_{10}$ (Table I, sample 16) for the superconducting phase. This implies either that the oxidation states of some of the bismuth or copper in this compound are Bi^{5+} or Cu^{3+}, respectively, or some of the oxygen is present as peroxide.

The results concerning the bismuth and thallium superconductors are different from the general belief that their oxygen stoichiometry is very near to 8, which would correspond to formal charges of Cu^{2+}, Tl^{3+}, and

Bi^{3+}. Nevertheless, as pointed out in the introduction, their oxygen content has not been fully elucidated prior to this work. The oxygen surplus found is in good agreement with many other observations, as discussed below. The $Bi_2CaSr_2Cu_2O_{10}$ stoichiometry proposed based on the TPR results eliminates, for example, the contradiction between the existence of Bi^{5+}, Cu^{3+}, and O^- reported for these compounds (*21, 50, 59–62*), and their supposed O_8-type oxygen stoichiometry. The observed "excess" oxygen in the double BiO or TlO layers (*21, 31, 33, 36, 64*) is also in good agreement with the high oxygen content, but is difficult to explain on the basis of Cu^{2+} and Bi^{3+} formal oxidation states. Crystallographic calculations showed (*65*) that the bismuth superconductor can accomodate as many as two extra oxygens per formula unit. Our TPR result can be considered to be the first experimental proof for preparation of a fully oxidized $Bi_2CaSr_2Cu_2O_{10}$ sample.

The already high oxygen content of bismuth and thallium superconductors makes it easy to understand why these compounds did not adsorb oxygen even at elevated pressures, in contrast to $YBa_2Cu_3O_{6.5+x}$ which is not fully oxidized (*21, 33*). As mentioned in the introduction, the presence of mixed valence states is supposed to be one of the most important factors for high temperature superconductivity (*21, 50*). For the $YBa_2Cu_3O_{6.5+x}$ superconductor, oxygen treatment is required to get more O^-- or Cu^{3+}-type ions, in addition to O^{2-} or Cu^{2+}. In contrast, mixed valence states in the fully oxidized bismuth and thallium superconductors with formal charges of Bi^{5+}, Tl^{3+}, and Cu^{3+} can appear after reduction. This is in good agreement with experimental results for the effect of oxygen on superconductivity: increasing the oxygen content of $YBa_2Cu_3O_{6.5+x}$ increases its T_c (*21, 22, 26*), while in the other two groups of superconductors the removal of oxygen resulted in increasing T_c (*32, 33, 37, 39*). These behaviors of superconductors can probably be explained by changes in hole density (*24, 25, 33, 39, 85*).

Acknowledgments

The authors thank Dr. L. E. Wenger and Dr. W. Wyn for the magnetic measurements on superconducting samples. We are also grateful for a grant from Ford Motor Co. to the Institute for Manufacturing Research at Wayne State University to support this research. A. Brenner and H.-W. Jen gratefully acknowledge support from the Department of Energy, Office of Basic Energy Sciences.

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