(reactions 20 and 21). It is noteworthy that with each complex, both $\mathrm{Metal^{II}{\cdot}L{\cdot}X}$ and $\mathrm{Metal^{II}{\cdot}X_2}$ follow the same ionization patterns as $\mathrm{Metal^{II}{\cdot}L_2}$. Thus, $\mathrm{Cu^{II}{\cdot}L_2}$, $\mathrm{Cu^{II}{\cdot}L{\cdot}X}$, and $\mathrm{Cu^{II}{\cdot}X_2}$ all tend to favor ionization by resonance electron capture whereas ionization of $\mathrm{Zn^{II}{\cdot}L_2}$, $\mathrm{Zn^{II}{\cdot}L{\cdot}X}$, and $\mathrm{Zn^{II}{\cdot}X_2}$ occurs exclusively by ion/molecule processes.

The absence of $\mathrm{[Metal^{II}{\cdot}F_3]^-}$, $\mathrm{[Metal^{I}{\cdot}L{\cdot}F]^-}$, and $\mathrm{[Metal^{I}{\cdot}F_2]^-}$ ions in the NF_3 NCI mass spectra suggests that atomic fluorine may have reaction channels open to it, such as hydrogen atom abstraction, that are more exothermic than the ligand displacement channel. Again, by use of the reaction with acetone as a guide to the likely enthalpy of the reactions involving the metal complexes, it is calculated that abstraction of a methyl hydrogen atom from acetone by $F^{\bullet}$ is exothermic by 38.0 kcal mol^{-1}.[22] This is substantially more exothermic than the enthalpy values calculated for the displacement of an acetylacetonate radical from the complexes by $F^{\bullet}$, which fall in the range −20.6 to −31.7 kcal mol^{-1}.[22] Consequently, some of the $\mathrm{[Metal^{II}{\cdot}L_2 - H]^-}$ ions formed in the NF_3 plasma may arise due to hydrogen atom abstraction followed by resonance electron capture.

Formation of ions of the type $\mathrm{[Metal^{I}{\cdot}L_2X - H]^-}$ and $\mathrm{[Metal^{II}{\cdot}L_2{\cdot}X_2 - H]^-}$ indicates that halogen radicals also react with the metal complexes by an alternative reaction pathway involving homolytic substitution at a ligand methine carbon,[13] reaction 22. This produces a molecule of the form $\mathrm{(Metal^{II}{\cdot}L_2{\cdot}X - H)}$, which may be ionized by resonance electron capture or nucleophilic halide addition to form $\mathrm{[Metal^{I}{\cdot}L_2{\cdot}X - H]^-}$ and $\mathrm{[Metal^{II}{\cdot}L_2{\cdot}X_2 - H]^-}$, respectively (reactions 23 and 24).

As CF_2Cl_2 and CF_3Br plasmas contain populations of the halogenated methyl radicals $^{\bullet}CF_2Cl$ and $^{\bullet}CF_3$, respectively, formation of the ions $\mathrm{[Metal^{II}{\cdot}L_2{\cdot}R]^-}$ and $\mathrm{[Metal^{III}{\cdot}L_2{\cdot}R{\cdot}X]^-}$, where R corresponds to CF_2Cl in the CF_2Cl_2 NCI mass spectra and CF_3 in the CF_3Br spectra, is attributed to radical/molecule reactions involving these halogenated methyl radicals. The adduct ions are observed only in the mass spectra of the cobalt complex. In a previous study[7,8] we demonstrated that certain cobalt(II) complexes including bis(acetylacetonato)cobalt(II) trap alkyl radicals in methane NCI plasmas to produce alkyl adduct molecules, which may be ionized to yield alkyl adduct negative ions. One-electron oxidative addition of an alkyl radical to the metal followed by resonance electron capture ionization of the product was indicated as the source of the alkyl adduct ions. Oxidative addition of halogenated methyl radicals to the cobalt complex in the CF_2Cl_2 and CF_3Br plasmas, reaction 25, is clearly analogous to the addition of methyl and other alkyl radicals in methane NCI plasmas. Ionization of the five-coordinate $\mathrm{Metal^{III}{\cdot}L_2{\cdot}R}$ molecule by resonance electron capture produces $\mathrm{[Metal^{II}{\cdot}L_2{\cdot}R]^-}$, while nucleophilic halide addition yields six-coordinate $\mathrm{[Metal^{III}{\cdot}L_2{\cdot}R{\cdot}X]^-}$ (reactions 26 and 27). This reaction sequence is prevalent with the cobalt complex because of the accessibility of the cobalt +3 oxidation state.

Cluster ions of the form $\mathrm{[Metal^{II}{}_x{\cdot}L_y{\cdot}X_z]^-}$ ($x = 2$ or 3; $y + z = 2x + 1$) are a further feature of the mass spectra. These ions are most prominent in the CF_2Cl_2 and CF_3Br mass spectra of the zinc complex, and their occurrence may be explained in terms of ion/molecule reactions between metal-containing ions and neutrals in the plasmas. For example, clustering of $\mathrm{[Metal^{II}{\cdot}L_2{\cdot}X]^-}$ with $\mathrm{Metal^{II}{\cdot}L_2}$, $\mathrm{Metal^{II}{\cdot}L{\cdot}X}$, and $\mathrm{Metal^{II}{\cdot}X_2}$ accounts for the formation of $\mathrm{[Metal^{II}{}_2{\cdot}L_4{\cdot}X]^-}$, $\mathrm{[Metal^{II}{}_2{\cdot}L_3{\cdot}X_2]^-}$, and $\mathrm{[Metal^{II}{}_2{\cdot}L_2{\cdot}X_3]^-}$, respectively. Further clustering of these ions is the probable source of ions containing three metal atoms. Formation of these clusters indicates the presence of neutral species such as $\mathrm{Metal^{II}{\cdot}X_2}$ in the plasmas.

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Registry No. $\mathrm{Co^{II}{\cdot}L_2}$, 14024-48-7; $\mathrm{Ni^{II}{\cdot}L_2}$, 3264-82-2; $\mathrm{Cu^{II}{\cdot}L_2}$, 13395-16-9; $\mathrm{Zn^{II}{\cdot}L_2}$, 14024-63-6; NF_3, 7783-54-2; CF_2Cl_2, 75-71-8; CF_3Br, 75-63-8; $[F]^-$, 16984-48-8; $[Cl]^-$, 16887-00-6; $[Br]^-$, 24959-67-9; CF_2Cl, 1691-89-0; CF_3, 2264-21-3; proton, 12408-02-5; hydrogen, 1333-74-0.

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Thermochemistry of Rare-Earth-Metal–Alkaline-Earth-Metal–Copper Oxide Superconductors[†]

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Enthalpies of formation of the perovskite-related oxides La_2CuO_4, $La_{1.85}Sr_{0.15}CuO_4$, and $YBa_2Cu_3O_y$ (y = 6.25, 6.47, 6.69, and 6.93) have been determined at 298.15 K by solution calorimetry. Room-temperature stabilities of these compounds have been assessed in terms of the parent binary oxides and of the oxygen content. High-temperature (to 900 °C) thermal behavior of $YBa_2Cu_3O_y$ has been used to determine thermodynamic properties (partial molal enthalpy, free energy, and entropy of oxygen) of this material in order to characterize the quenched state in relation to the high-temperature equilibrium state. The thermochemistry of oxygen has been used to interpret the relationship between the oxygen partial pressure and the defect chemistry in the nonstoichiometric phase of $YBa_2Cu_3O_y$. The relevance of the defect chemistry to conductivity is discussed.

Introduction

It has sometimes been asserted that the stability of a complex oxide or fluoride (as opposed to a double oxide or fluoride, the difference being the ability to identify a discrete polyatomic cluster in a complex compound) is greater than the sum of the parent binary oxides by virtue of a larger Madelung constant[1] or because of an acid–base difference in the parent oxides.[2] It is also often observed that cations of high oxidation state can be stabilized in complex salts.[3] The ease of preparation of the two classes of high-temperature superconducting oxides now known,[4] at least to the degree of purity defined by single-phase X-ray powder

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diffraction patterns, indicates that at high temperatures (500–950 °C) these complex oxides (e.g. La_2CuO_4 and $YBa_2Cu_3O_{6.5}$) must be more stable than the parent binary oxides (La_2O_3, CuO, etc.). Nevertheless, it is still important to know how much more stable these complex oxides are at high temperatures. It is also important to determine whether these materials are indeed stable or metastable at ambient temperature and how unstable they are with respect to hydroxides, carbonates, peroxides, etc., since there is evidence that atmospheric gases[5–7] and water[8,9] attack them.

To determine the enthalpies of formation by solution calorimetry, it is necessary to use samples prepared at high temperature but quenched to room temperature. Such samples may not be representative of an equilibrium state. Therefore, it is important to compare thermochemical quantities determined from equilibrium measurements with those determined with the quenched samples. Since equilibrium oxygen vapor pressures over $YBa_2Cu_3O_y$ have been measured as a function of y by TGA,[10–14] EMF,[15] and neutron diffraction,[16] such a comparison can be made if the calorimetric enthalpy of solution is determined with samples containing various oxygen content in the quenched samples.

If the quenched samples do in fact represent the equilibrium state, then the defect chemistry implied by the variation of the partial oxygen vapor pressure with composition and temperature can be used to interpret the conductivities. The roles of valence state involved in the defect chemistry can accordingly be identified.

Experimental Section

Preparation of Samples. La_2CuO_4 and $La_{1.85}Sr_{0.15}CuO_4$ were prepared from 1.00 M nitrate solutions that had been prepared by weighing La_2O_3 (99.9%, calcined to 900 °C), $SrCO_3$ (99.999%), or Cu (99.99%), dissolving each in dilute nitric acid, and then adjusting to an accurately known volume. Each metal nitrate solution was dispensed volumetrically, the mixed solution was evaporated slowly to dryness, and the resulting solid was pulverized, heated to 400 °C, pulverized again, heated to 950 °C in air for 12 h, ground thoroughly, and reheated and reground twice again. Samples were furnace cooled in air. $YBa_2Cu_3O_{6.93}$ was prepared from Y_2O_3 (99.9%, calcined to 900 °C), $BaCO_3$ (99.999%), and CuO (99.9%, prepared by thermal decomposition of cupric acetate to 650 °C in O_2, with Cu content assayed by TGA reduction in H_2 and also by iodometric assay[17]); the powders were weighed out, thoroughly mixed, ground, heated to 950 °C rapidly, and held there for 12 h in air, cooled, reground, and heated to 960 °C for 24 h in air, cooled, reground, and heated to 900 °C in O_2 for 2 h, and cooled slowly (6 h) to room temperature in O_2. Pellets of this last material were prepared by mulling with 1% tetraethylene glycol in methanol, pressing disks at 20 000 psi, and reheating in O_2 as above. $YBa_2Cu_3O_{6.69}$ and $YBa_2Cu_3O_{6.47}$ were prepared by heating these pellets in air at 775 and 856 °C, respectively, and quenching them. $YBa_2Cu_3O_{6.25}$ was prepared by heating powdered $YBa_2Cu_3O_{6.93}$ in 1% O_2–99% N_2 to 850 °C and cooling rapidly (100 °C/min). Oxygen contents were determined by the method of Appelman et al.[17] Each sample was found to be single phase by X-ray powder diffraction: $YBa_2Cu_3O_{6.93}$ and $YBa_2Cu_3O_{6.69}$ were orthorhombic and $YBa_2Cu_3O_{6.47}$ and $YBa_2Cu_3O_{6.25}$ were tetragonal as expected.[16]

Table I. Enthalpies of Solution in 4.00 M $HClO_4$(aq) at 298.15 K

compd	mass/mg	enthalpy/J	$\Delta_{soln}H/(kJ\ mol^{-1})$	
La_2CuO_4	41.8	51.94		−503.7
	53.3	66.21		−503.5
	55.6	67.20		−489.9
	50.94	64.18		−510.7
	68.27	87.56		−519.9
	36.08	46.05		−517.5
	69.83	88.15		−511.7
			mean	−508.1 ± 10.2
$La_{1.85}Sr_{0.15}CuO_4$	46.3	58.35		−501.2
	49.3	61.65		−497.3
	50.5	63.68		−501.5
	45.4	57.98		−506.7
			mean	−501.7 ± 3.9
$YBa_2Cu_3O_{6.93}$	186.63	225.84		−804.8
	185.39	221.91		−796.1
	223.28	271.16		−808.0
	69.78	84.52		−805.6
	87.14	104.80		−799.9
			mean	−802.9 ± 4.8
$YBa_2Cu_3O_{6.69}$	75.75	95.14		−829.0
	100.48	125.47		−824.3
	76.76	96.70		−831.6
	87.88	109.63		−823.5
			mean	−827.1 ± 3.9
$YBa_2Cu_3O_{6.47}$	56.81	72.72		−840.6[a]
	94.72	120.60		−836.2[a]
	94.16	121.22		−845.5
	89.01	115.44		−851.8
	130.29	168.66		−850.2
			mean	−844.9 ± 6.5
$YBa_2Cu_3O_{6.25}$	78.03	103.06		−858.7[b]
	48.42	63.93		−858.5[b]
	54.33	71.75		−858.7[b]
	41.09	53.82		−851.7[b]
			mean	−856.9 ± 3.5
Y_2O_3	70.51	114.26		−365.9
	76.04	123.09		−365.5
			mean	−365.7 ± 2.0
La_2O_3	71.35	100.27		−457.9
	64.37	90.86		−459.9
			mean	−458.9 ± 3.0
$Ba(ClO_4)_2 \cdot 3H_2O$	134.35	11.2		+33.24
	202.91	17.50		+33.7
	219.69	17.0		+30.1
			mean	+32.1 ± 3.6
$SrCO_3$	99.06	11.47		−17.1
	131.16	15.30		−17.2
			mean	−17.2 ± 1.0

[a] In 4.00 M $HClO_4$–0.001 M Br_2(aq). [b] In 4.00 M $HClO_4$–0.010 M $(NH_4)_2Ce(NO_3)_6$(aq).

All other reagents were of the highest purity available. $Ba(ClO_4)_2 \cdot 3H_2O$ was synthesized by recrystallization of a hot saturated solution made by neutralizing $Ba(OH)_2$ with $HClO_4$. It was analyzed gravimetrically for Ba. Anal. Calcd for $Ba(ClO_4)_2 \cdot 3H_2O$: Ba, 35.19. Found: Ba, 34.94.

Calorimetry. A medium of 4.00 M $HClO_4$(aq) (reagent grade) was chosen after several trials of more dilute acid since it dissolves the superconducting oxides readily, since it contains no reducing agents, and since it cannot be oxidized. For $YBa_2Cu_3O_{6.25}$, which dissolves in $HClO_4$ with a precipitate (probably Cu from disproportionation of Cu^+), the medium was 4.00 M $HClO_4$–0.010 M Ce(IV), where the Ce(IV) was obtained from dissolution of $(NH_4)_2Ce(NO_3)_6$ (GFS Chemicals, 99.9%). Samples were stored under dry N_2 until ready to use, pulverized to fine granules, and weighed in air ($YBa_2Cu_3O_{6.25}$ was handled and weighed in a nitrogen-filled drybox) on a semimicro balance into glass ampules, which were then sealed with glass plugs and Apiezon W wax. Four ampules were loaded onto a holder mounted on the stirring shaft so that each could be broken individually by stopping the stirrer and indexing the shaft so that the ampule was above a carborundum chip affixed to the calorimeter baffle. In other respects the calorimeter was the same as previously described.[18]

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Results

The calorimetric scheme for $\Delta_f H^\circ(La_2CuO_4,s)$ is described by eq 1–7, which have been written so as to sum to eq 8, corresponding to the formation of La_2CuO_4. In all of these equations, "soln" refers to 4.00 M $HClO_4(aq)$. Reactions for ΔH_1, ΔH_3, ΔH_9, ΔH_{11}, ΔH_{14}, ΔH_{17}, ΔH_{18}, and ΔH_{20} are those measured in this research (Table I).

$2La(ClO_4)_3(soln) + Cu(ClO_4)_2(soln) + 4H_2O(soln) = La_2CuO_4(s) + 8HClO_4(soln)$ (1)

$\Delta H_1 = +508.1 \pm 10.2$ kJ mol^{-1}

$2La(s) + {}^3/_2O_2(g) = La_2O_3(s)$ (2)

$\Delta H_2 = -1793.7 \pm 2.0$ kJ mol^{-1} [19]

$La_2O_3(s) + 6HClO_4(soln) = 2La(ClO_4)_3(soln) + 3H_2O(soln)$ (3)

$\Delta H_3 = -458.9 \pm 3.0$ kJ mol^{-1}

$Cu(s) + Cl_2(g) + 7O_2(g) + 6H_2(g) = Cu(ClO_4)_2 \cdot 6H_2O(s)$ (4)

$\Delta H_4 = -1928.4 \pm 3.0$ kJ mol^{-1} [19]

$Cu(ClO_4)_2 \cdot 6H_2O(s) = Cu(ClO_4)_2(soln) + 6H_2O(soln)$ (5)

$\Delta H_5 = 5.7 \pm 0.2$ kJ mol^{-1} [20]

$2HClO_4(soln) = H_2(g) + Cl_2(g) + 4O_2(g)$ (6)

$2\Delta H_6 = 2(+127.1 \pm 1.0)$ kJ mol^{-1} [21]

$5H_2O(soln) = 5H_2(g) + {}^5/_2O_2(g)$ (7)

$5\Delta H_7 = 5(+286.10 \pm 0.05)$ kJ mol^{-1} [21]

net: $2La(s) + Cu(s) + 2O_2(g) = La_2CuO_4(s)$ (8)

$\Delta H_8 = \Delta_f H^\circ = -1983 \pm 14$ kJ mol^{-1}

The calorimetric scheme for $La_{1.85}Sr_{0.15}CuO_4$ is given in eq 9–13.

$1.85La(ClO_4)_3(soln) + 0.15Sr(ClO_4)_2(soln) + Cu(ClO_4)_2(soln) + 3.925H_2O(soln) = La_{1.85}Sr_{0.15}CuO_4(s) + 7.85HClO_4(soln)$ (9)

$\Delta H_9 = +501.7 \pm 3.9$ kJ mol^{-1}

$1.85La(s) + 1.3875O_2(g) = 0.925La_2O_3(s)$

$0.925\Delta H_2 = 0.925(-1793.7 \pm 2.0)$ kJ mol^{-1} [19]

$0.925La_2O_3(s) + 5.55HClO_4(soln) = 1.85La(ClO_4)_3(soln) + 2.775H_2O(soln)$

$0.925\Delta H_3 = 0.925(-458.9 \pm 3.0)$ kJ mol^{-1}

$Cu(s) + Cl_2(g) + 7O_2(g) + 6H_2(g) = Cu(ClO_4)_2 \cdot 6H_2O(s)$

$\Delta H_4 = -1928.4 \pm 3.0$ kJ mol^{-1} [19]

$Cu(ClO_4)_2 \cdot 6H_2O(s) = Cu(ClO_4)_2(soln) + 6H_2O(soln)$

$\Delta H_5 = 5.7 \pm 0.2$ kJ mol^{-1} [20]

$2HClO_4(soln) = H_2(g) + Cl_2(g) + 4O_2(g)$

$\Delta H_6 = 2(+127.1 \pm 1.0)$ kJ mol^{-1} [21]

$5H_2O(soln) = 5H_2(g) + {}^5/_2O_2(g)$

$\Delta H_7 = 5(+286.10 \pm 0.05)$ kJ mol^{-1} [21]

$0.15Sr(s) + 0.15C(s) + 0.225O_2(g) = 0.15SrCO_3(s)$ (10)

$\Delta H_{10} = 0.15(-1225.8 \pm 1.1)$ kJ mol^{-1} [22]

$0.15SrCO_3(s) + 0.3HClO_4(soln) = 0.15Sr(ClO_4)_2(soln) + 0.15CO_2(g) + 0.15H_2O(soln)$ (11)

$\Delta H_{11} = -0.15(17.2 \pm 1.0)$ kJ mol^{-1}

$0.15CO_2(g) = 0.15C(s) + 0.15O_2(g)$ (12)

$\Delta H_{12} = 0.15(+393.51 \pm 0.13)$ kJ mol^{-1} [19]

net: $1.85La(s) + 0.15Sr(s) + Cu(s) + 2O_2(g) = La_{1.85}Sr_{0.15}CuO_4(s)$ (13)

$\Delta H_{13} = \Delta_f H^\circ = -1947 \pm 6$ kJ mol^{-1}

The calorimetric scheme for $YBa_2Cu_3O_{6.93}$ is given in eq 14–19.

$Y(ClO_4)_3(soln) + 2Ba(ClO_4)_2(soln) + 3Cu(ClO_4)_2(soln) + 0.215O_2(g) + 6.5H_2O(soln) = YBa_2Cu_3O_{6.93}(s) + 13HClO_4(soln)$ (14)

$\Delta H_{14} = +802.9 \pm 4.8$ kJ mol^{-1}

$Y(s) + 0.75O_2(g) = 0.5Y_2O_3(s)$ (15)

$\Delta H_{15} = 0.5(-1905.6 \pm 2.0)$ kJ mol^{-1} [23]

$2Ba(s) + 2Cl_2(g) + 11O_2(g) + 6H_2(g) = 2[Ba(ClO_4)_2 \cdot 3H_2O(s)]$ (16)

$\Delta H_{16} = 2(-1691.6 \pm 3)$ kJ mol^{-1} [19]

$2[Ba(ClO_4)_2 \cdot 3H_2O(s)] = 2Ba(ClO_4)_2(soln) + 6H_2O(soln)$ (17)

$\Delta H_{17} = 2(+32.1 \pm 3.6)$ kJ mol^{-1}

$3Cu(s) + 3Cl_2(g) + 21O_2(g) + 18H_2(g) = 3[Cu(ClO_4)_2 \cdot 6H_2O(s)]$

$3\Delta H_4 = 3(-1928.4 \pm 1.0)$ kJ mol^{-1} [19]

$3[Cu(ClO_4)_2 \cdot 6H_2O(s)] = 3Cu(ClO_4)_2(soln) + 18H_2O(soln)$

$3\Delta H_5 = 3(+5.7 \pm 0.2)$ kJ mol^{-1} [20]

$0.5Y_2O_3(s) + 3HClO_4(soln) = Y(ClO_4)_3(soln) + 1.5H_2O(soln)$ (18)

$\Delta H_{18} = 0.5(-365.7 \pm 2.0)$ kJ mol^{-1}

$10HClO_4(soln) = 5H_2(g) + 5Cl_2(g) + 20O_2(g)$

$10\Delta H_6 = 10(127.1 \pm 1.0)$ kJ mol^{-1} [21]

$19H_2O(soln) = 19H_2(g) + 9.5O_2(g)$

$19\Delta H_7 = 19(286.10 \pm 0.5)$ kJ mol^{-1} [21]

net: $Y(s) + 2Ba(s) + 3Cu(s) + 3.465O_2(g) = YBa_2Cu_3O_{6.93}(s)$ (19)

$\Delta H_{19} = \Delta_f H^\circ = -2713 \pm 17$ kJ mol^{-1}

Similar thermochemical equations yield $\Delta_f H^\circ(YBa_2Cu_3O_{6.69},s) = -2689 \pm 17$ kJ mol^{-1} and $\Delta_f H^\circ(YBa_2Cu_3O_{6.47},s) = -2671 \pm 18$ kJ mol^{-1}.

The calorimetric scheme for $YBa_2Cu_3O_{6.25}$ is given in eq 20–22.

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$$\mathrm{Y(ClO_4)_3(soln) + 2Ba(ClO_4)_2(soln) + 3Cu(ClO_4)_2(soln) + 0.5Ce(ClO_4)_3(soln) + 6.25H_2O(soln) = YBa_2Cu_3O_{6.25}(s) + 0.5Ce(ClO_4)_4(soln) + 12.5HClO_4(soln)} \quad (20)$$

$$\Delta H_{20} = +856.9 \pm 3.5\ \mathrm{kJ\ mol^{-1}}$$

$$\mathrm{Y(s) + 0.75O_2(g) = 0.5Y_2O_3(s)}$$

$\Delta H_{15} = 0.5(-1905.6 \pm 2.0)\ \mathrm{kJ\ mol^{-1}}$ [23]

$$\mathrm{2Ba(s) + 2Cl_2(g) + 11O_2(g) + 6H_2(g) = 2[Ba(ClO_4)_2{\cdot}3H_2O(s)]}$$

$\Delta H_{16} = 2(-1691.6 \pm 3.0)\ \mathrm{kJ\ mol^{-1}}$ [19]

$$\mathrm{2[Ba(ClO_4)_2{\cdot}3H_2O(s)] = 2Ba(ClO_4)_2(soln) + 6H_2O(soln)}$$

$$\Delta H_{17} = 2(+32.1 \pm 3.6)\ \mathrm{kJ\ mol^{-1}}$$

$$\mathrm{3Cu(s) + 3Cl_2(g) + 21O_2(g) + 18H_2(g) = 3[Cu(ClO_4)_2{\cdot}6H_2O(s)]}$$

$3\Delta H_4 = 3(-1928.4 \pm 1.0)\ \mathrm{kJ\ mol^{-1}}$ [19]

$$\mathrm{3[Cu(ClO_4)_2{\cdot}6H_2O(s)] = 3Cu(ClO_4)_2(soln) + 18H_2O(soln)}$$

$3\Delta H_5 = 3(+5.7 \pm 0.2)\ \mathrm{kJ\ mol^{-1}}$ [20]

$$\mathrm{0.5Y_2O_3(s) + 3HClO_4(soln) = Y(ClO_4)_3(soln) + 1.5H_2O(soln)}$$

$$\Delta H_{18} = 0.5(-365.7 \pm 3.0)\ \mathrm{kJ\ mol^{-1}}$$

$$\mathrm{10HClO_4(soln) = 5H_2(g) + 5Cl_2(g) + 20O_2(g)}$$

$10\Delta H_6 = 10(127.1 \pm 1.0)\ \mathrm{kJ\ mol^{-1}}$ [21]

$$\mathrm{19.25H_2O(soln) = 19.25H_2(g) + 9.625O_2(g)}$$

$19.25\Delta H_7 = 19.25(286.10 \pm 0.5)\ \mathrm{kJ\ mol^{-1}}$ [21]

$$\mathrm{{}^1/_2Ce(ClO_4)_4(soln) + {}^1/_4H_2(g) = {}^1/_2Ce(ClO_4)_3(soln) + {}^1/_2HClO_4(soln)} \quad (21)$$

$\Delta H_{21} = 0.5(-166.4 \pm 2.0)\ \mathrm{kJ\ mol^{-1}}$ [24]

$$\text{net:}\quad \mathrm{Y(s) + 2Ba(s) + 3Cu(s) + 3.125O_2(g) = YBa_2Cu_3O_{6.25}(s)} \quad (22)$$

$$\Delta H_{22} = \Delta_f H^\circ = -2671 \pm 17\ \mathrm{kJ\ mol^{-1}}$$

Calculations

From the standard enthalpies of formation, it is possible to calculate the enthalpies of formation of these complex oxides with respect to the parent binary oxides (eq 23 and 24). For these

$$\mathrm{La_2O_3(s) + CuO(s) = La_2CuO_4(s)} \quad (23)$$

$$\Delta H_{23}{}^\circ = -28\ \mathrm{kJ\ mol^{-1}}$$

$$\mathrm{{}^1/_2Y_2O_3(s) + 2BaO(s) + 3CuO(s) = YBa_2Cu_3O_{6.5}(s)} \quad (24)$$

$$\Delta H_{24}{}^\circ = -143\ \mathrm{kJ\ mol^{-1}}$$

calculations we have used $\Delta_f H^\circ(\mathrm{BaO,s}) = -548.0 \pm 2.0$ kJ mol^{-1} [25] and $\Delta_f H^\circ(\mathrm{CuO,s}) = -161.5 \pm 0.8$ kJ mol^{-1}.[26] In the latter case, $\Delta_f H^\circ(\mathrm{YBa_2Cu_3O_{6.5}(s)})$ was estimated to be -2675 ± 20 kJ mol^{-1} by interpolation between $y = 6.69$ and $y = 6.47$. Since entropy changes for solid-state reactions are very small, the enthalpies of these reactions may be used to argue that these complex oxides, especially $\mathrm{YBa_2Cu_3O}_y$, are more stable than the parent binary oxides. The large negative enthalpy of formation of the latter compound from binary oxides is due in large measure to the high basicity and instability of BaO.

Table II. Partial Molar Enthalpy and Entropy of Solution of O_2 in $\mathrm{YBa_2Cu_3O}_y$[a]

y	$-\Delta H/(\mathrm{kJ\ mol^{-1}})$	$-\Delta S/(\mathrm{J\ mol^{-1}\ K^{-1}})$	ref
6.3	189	151	10
	211	169	11
	152	120	12
	139	109	13
	238		14
	151	120	15
6.5	208	195	10
	215	201	11
	149	136	12
	149	139	13
	224	189	14
	138	130	15
6.7	211	222	10
	219	235	11
	162	172	12
	166	181	13
	200		14
	190		*b*

[a] Reaction is $\lim_{a\to\infty} [a\mathrm{YBa_2Cu_3O}_y\mathrm{(s)} + {}^1/_2\mathrm{O_2(g)} \rightarrow a\mathrm{YBa_2Cu_3O}_{y+1/a}]$. [b] This research.

Evidence is accumulating that these superconducting oxides are unstable with respect to atmospheric H_2O and CO_2.[5–9] A typical reaction is given in eq 25, where the products are the stable

$$\mathrm{La_2CuO_4(s) + (\mathit{x} + 0.5)H_2O(g) + 3.5CO_2(g) = La_2(CO_3)_3{\cdot}\mathit{x}H_2O + 0.5[CuCO_3{\cdot}Cu(OH)_2]} \quad (25)$$

lanthanum carbonate and the basic copper carbonate malachite. For this reaction we are fortunate to have the entropy of $\mathrm{La_2CuO_4(s)}$ (178.1 ± 0.2 J K^{-1} mol^{-1} [27]) as well as the free energy of formation of lanthanum carbonate and of malachite,[19] so that we calculate $\Delta_f G^\circ(\mathrm{La_2CuO_4,s}) = -1870$ kJ mol^{-1}. We note that high-temperature emf measurements have already been made[28] on $\mathrm{La_2CuO_4}$; although the extrapolation of these measurements to room temperatue is unreliable, it does lead to a good agreement with our estimate, -1919 kJ mol^{-1}. For the above decomposition reaction we calculate $\Delta G^\circ = -224$ kJ mol^{-1}, which shows that $\mathrm{La_2CuO_4}$ is quite unstable with respect to gaseous constituents of air.

For the similar reaction

$$\mathrm{YBa_2Cu_3O_{6.93}(s) + 1.5H_2O(g) + 5CO_2(g) = 0.5Y_2(CO_3)_3(s) + 2BaCO_3(s) + 1.5[CuCO_3{\cdot}Cu(OH)_2] + 0.215O_2(g)} \quad (26)$$

we estimate $S^\circ(\mathrm{YBa_2Cu_3O_{6.93},s,298\ K}) = 330$ J K^{-1} mol^{-1}; from heat capacity measurements[29] we find a value of 332 J K^{-1} mol^{-1}. Hence we calculate $\Delta_f G^\circ(\mathrm{YBa_2Cu_3O_{6.93},s}) = -2520$ kJ mol^{-1}. Using literature enthalpies and free energies of formation,[19] we calculate $\Delta G^\circ = -355$ kJ mol^{-1} for the above decomposition reaction, again strongly confirming the instability of these compounds with respect to water vapor and CO_2.

The values for the enthalpies of formation for the $\mathrm{YBa_2Cu_3O}_y$ phase show a variation with oxygen content. One obtains a value of -190 kJ (mol of O_2)$^{-1}$ for the partial molar enthalpy of solution of oxygen in the phase. This value can be compared with that obtained from equilibration measurements at high temperatures.

Thermochemistry of the Nonstoichiometric Phase $\mathrm{YBa_2Cu_3O}_y$

Isobaric TGA measurements have been made by several groups;[10–14] we have used these data to calculate partial pressures

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of oxygen in equilibrium with $YBa_2Cu_3O_y$ at temperatures from 350 to 900 °C. Unfortunately there is very poor consistency among these measurements, either because the solid samples were not single phase or because equilibrium conditions are difficult to reach at low $p(O_2)$ and moderate temperatures. From these partial pressures we have calculated partial molar enthalpies and entropies of solution of oxygen at these compositions. Plots of $\log p(O_2)$ vs T^{-1} are linear, so that the enthalpies and entropies have been derived from linear least-squares analyses. The values listed in Table II show that the partial molar enthalpy of solution of O_2 is ~ -200 kJ (mol of $O_2)^{-1}$ and the partial molar entropy varies between ~ -120 and ~ -200 J K^{-1} (mol of $O_2)^{-1}$ for the range from $y = 6.3$ to $y = 6.7$. Using the relative error of $\sim \pm 5$ kJ mol^{-1} in the calorimetric values, we find that a linear plot of $\Delta_{soln}H$ vs y between $y = 6.47$ and $y = 6.93$ gives a partial molar enthalpy of solution of -190 ± 20 kJ mol^{-1}, in agreement with that derived from equilibrium measurements. Differences attributable to frozen-in strains may exist, but more precise and extensive measurements are needed to detect strain effects if they are significant. Consequently, for the most part, the values indicate that the quenched samples correspond closely to the equilibrated samples in a thermochemical sense. Thus a thermochemical examination based on the high-temperature data can be useful in understanding the defect chemistry with respect to the superconducting state. In this sense, the phase may be said to be metastable, a condition frequently discussed in relation to the state.[30]

Beginning with the discovery that reduced strontium titanate is superconducting and continuing with the recent investigations of the $YBa_2Cu_3O_{7-\delta}$ phase, the role of nonstoichiometry has been recognized. However, little if any discussion of this role on the basis of the thermochemistry has been presented. The following discussion attempts to identify this role even though a quantitative evaluation of the nonstoichiometry in terms of the valence states and the lattice defect energies cannot yet be presented.

If a phase does contain distinguishable Cu cations (the Cu(1) of Jorgensen et al.[16]) of different charge states, then the partial vapor pressure of oxygen in equilibrium with the phase can be represented by eq 27, in which cs and as represent cation and anion

$$O^{2-}as + 2Cu^{3+}cs = {}^1/_2O_2(g) + 2Cu^{2+}cs + as \qquad (27)$$

sites, respectively. By writing O^{2-}, Cu^{2+}, and Cu^{3+}, we do not mean to imply that the phase contains exactly these ions, but they are written this way to represent different charge states in the covalently bonded Cu–O conductive part of the solid. For the equilibrium constant, K, expressed in terms of these nominal concentrations, one can write

$$K = \frac{(n_{O_2}/V)^{1/2}(Cu^{2+}cs)^2(as)}{(Cu^{3+}cs)^2(O^{2-}as)} \qquad (28)$$

Rearranging with $n_{O_2}/V = P_{O_2}/RT$

$$P_{O_2}{}^{1/2} = (RT)^{1/2}K\frac{(Cu^{3+}cs)^2(O^{2-}as)}{(Cu^{2+}cs)^2(as)} \qquad (29)$$

$$\frac{1}{2}\ln P_{O_2} = \ln [(RT)^{1/2}K] + \ln\left[\frac{(Cu^{3+}cs)^2(O^{2-}as)}{(Cu^{2+}cs)(as)}\right] \qquad (30)$$

The values for the entropy given in Table II correspond to a change in the configurational entropy of ~ 15 J K^{-1} (mol of $O_2)^{-1}$ per 0.1 unit in y near 6.5. In eq 30, the configurational entropy is contained in the last term. Thus the experimental value is a measure of the incremental change in

$$2R\ln\left[\frac{(Cu^{3+}cs)^2(O^{2-}as)}{(Cu^{3+}cs)^2(as)}\right]$$

If this is the only equilibrium involved, then at $(Cu^{3+}cs) = 0$, $P_{O_2} = 0$, and the corresponding composition would be an insulator or a semiconductor with a large activation energy. Because the partial vapor pressures of oxygen at this assumed composition ($y = 6.5$) are relatively large (compared with zero), it appears that $(Cu^{3+}cs)$ is not zero and that, as TGA and EMF data demonstrate, an equilibrium involving three species (symbolized by Cu^+, Cu^{2+}, and Cu^{3+}) must be included. Thus the disproportionation reaction

$$2Cu^{2+}cs = Cu^{+}cs + Cu^{3+}cs \qquad (31)$$

may be involved. Consequently, for $y = 6.5$, the phase may contain Cu^+cs and $Cu^{3+}cs$ as well as $Cu^{2+}cs$.

Sleight has stated that the disproportionation is needed to produce the superconductive state.[30,31] One can certainly show that the disproportionation can lead to conductivity, but not necessarily to superconductivity. With the existence of the three nominal charge states, one can expect charge to be propagated in a network of Cu–Cu sites. In the absence of Cu^+ and Cu^{3+} no charge can be propagated along $(Cu^{2+}–Cu^{2+})_n$. However, if Cu^{3+} is introduced, charge can be transferred via the sequence $–Cu^{3+}–Cu^{2+}–Cu^{2+}– \rightarrow –Cu^{2+}Cu^{3+}–Cu^{2+}–$. But in this case, the composition with $\delta = 0.5$ ($y = 6.5$) would be an insulator. With both Cu^+ and Cu^{3+}, charge could propagate at $\delta < 0.5$, $\delta = 0.5$, and $\delta > 0.5$. Thus the sequence $(Cu^{2+}–Cu^{2+})_n \rightarrow (Cu^{+}–Cu^{3+}–Cu^{2+})_m \rightarrow (Cu^{+}–Cu^{2+}–Cu^{3+}–Cu^{2+})_m \rightarrow ...$ can occur. In this case the composition at $\delta = 0.5$ would be a semiconductor.

Although the mechanism for conduction along the Cu network seems plausible, it is not a likely one, because the distance between copper sites is relatively large. More likely, in this respect, is the propagation along the network of Cu–O sites. However, such can occur only if there are two possible and likely states for oxygen. To recognize such a possibility, one must recognize that the O^{2-} ion is stable only in an ionic environment where it is stabilized by the lattice self-energy. Because the Cu–O framework is covalently bonded, something other than the ionic O^{2-} alone is present. An examination of the photoelectron spectrum[32] of the Cu–O systems in the region of the valence band shows that the O(2p) and the Cu(3d) peaks are not resolved. Hence, the energies for $Cu^{2+}(3d^9)cs \rightarrow Cu^{3+}(3d^8)cs + e^-(g)$ and for $O^{2-}(2p^6)as \rightarrow O^-(2p^5)as + e^-(g)$ differ by a small amount. With the existence of Cu^{3+} and O^-, charge cannot be propagated in the network $(Cu^{2-}O^{2-})_n$, but if Cu^+ can occur, charge can be transferred.

The possibilities and the feasibilities cited above suggest that the nominal species needed in the phase for conductivity over the range of nonstoichiometry are Cu^+, Cu^{2+}, Cu^{3+}, O^{2-}, and O^-. In order for superconductivity to occur, however, some other conditions must be satisfied. These are the existence of the electron-pairing energy to form the diamagnetic state or the energy gap in the BCS theory[33] and the optimum concentration of carriers.[34]

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Registry No. La_2CuO_4, 12053-92-8; $La_{1.85}Sr_{0.15}CuO_4$, 107472-96-8; $YBa_2Cu_3O_{6.25}$, 111706-72-0; $YBa_2Cu_3O_{6.47}$, 111146-93-1; $YBa_2Cu_3O_{6.69}$, 110831-80-6; $YBa_2Cu_3O_{6.93}$, 112957-65-0; O_2, 7782-44-7; Y_2O_3, 1314-36-9; La_2O_3, 1312-81-8; $Ba(ClO_4)_2 \cdot 3H_2O$, 10294-39-0; $SrCO_3$, 1633-05-2.

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