

Reactivity of Y-Ba-Cu-O with binary oxides

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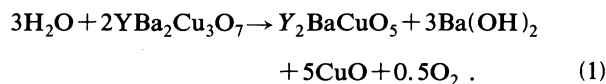
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The lattice O 1s binding energies of several binary oxides have been determined by x-ray photoelectron spectroscopy. They are found to be highly correlated with both the magnitude of the partial charge on oxygen and the dissociation energies of the oxides. It is suggested that the reaction of oxygen-deficient Y-Ba-Cu-O superconductor thin films with binary oxide substrates is acid-base in nature. Thus reactivity can be evaluated by the dissociation energy, by the magnitude of the partial charge on oxygen, or by the lattice O 1s binding energy of the binary oxide. As a rule, the reactivity increases with increasing dissociation energy, with decreasing magnitude of the partial charge on oxygen, and with increasing lattice O 1s binding energy of the binary oxide substrate.

INTRODUCTION

It is well known that chemical interactions between Y-Ba-Cu-O superconducting films and their substrates degrade the superconductivity. The extent of interaction depends strongly on the choice of substrate material; nevertheless, the nature of the interaction has not been fully clarified. Likewise, methods for evaluating the reactivity have not been fully developed. Koinuma *et al.*¹ have found that the Pauling electronegativity of a component in the substrate has a qualitative correlation with the reactivity of oxygen-deficient Y-Ba-Cu-O toward substrate materials, but this correlation does not seem to be very useful. Since the individual oxides of the metal ions in Y-Ba-Cu-O are basic oxides, it is reasonable to suggest that the Y-Ba-Cu-O substrate interaction should be predominantly acid-base in nature. Yan *et al.*² have suggested that the Y-Ba-Cu-O-water reaction occurs as follows:



Zhao *et al.*³ have reported that Ba, Sr, and Ca in superconducting Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O materials are moderately soluble in water and that pH jumps from about 6 to 11 within the first few minutes. In those experiments, powdered superconductor material has been dumped into deionized water at room temperature (0.275 g per 50 mL), and the pH has been monitored with time as the dispersion is gently stirred. These researchers isolated the aqueous phase and evaporated the water to give a residue of the dissolved material. For Y-Ba-Cu-O, only Ba(OH)₂ and trace amounts of copper oxides have been found, consistent with the fact that in Eq. (1) above, only Ba(OH)₂ is a strong electrolyte. Furthermore, the superconducting materials are very sensitive to atmospheric H₂O and CO₂, forming hydroxides and carbonates on the

surface. When Y-Ba-Cu-O is dumped into an acidic solution, significant oxygen evolution is observed, because the "copper oxide" component dissolves. Shafer *et al.*⁴ have recently shown that the evolved oxygen comes from lattice oxygen of the superconductor material and not from the solvent. They propose that the holes which exist in the oxygen-rich material are not due to Cu⁺³, but are due to lattice oxygens which occur as O⁻ or O₂²⁻. Oxidation-reduction (redox) behavior can be regarded as acid-base behavior in the Lewis sense, if the electrons are transferred in pairs. All of these results show that oxygen, in various forms, is important in the solid-solution interaction of these materials.

For thin films on solid substrates, the reactivity of interest occurs at the interface of the two solids, thus traditional acid-base theory, which has been used to explain successful interactions at the gas-solid or liquid-solid interface, is less useful in these cases. When the substrate is an oxide, the above results make attractive the use of oxide as a mediator. For example, O₂, O₂²⁻, and O²⁻ can be connected by the following equilibria:



Thus, the reaction of YBa₂Cu₃O_{6.5} with O₂ to give the p-type material could be regarded as occurring according to the reaction of O₂ with O²⁻ to produce O₂²⁻. Likewise, the decomposition of the oxygen-rich material in acid solution could be explained as the acid catalyzed disproportionation of O₂²⁻. Furthermore, the basicity of an oxide could be regarded as being modified by the cation(s). Thus, physical properties such as the partial charge on oxygen and the dissociation energy of the oxide become possible measures of basicity. Since the binding energy of the O 1s peak is expected to be a function of the partial charge on oxygen, it too becomes a possible measure of basicity. Any of these measures which show a

high correlation with the experimentally observed reactivity of Y-Ba-Cu-O films with oxide substrates can become the basis of a method for quantitatively assessing reactivity. The investigation of such correlations is the subject of this paper.

EXPERIMENTAL

The binary oxides examined in this study are powders of BaO, SrO, CaO, MgO, ZrO₂, Al₂O₃, and SiO₂ with analytical reagent or chemically pure purity. The Y-Ba-Cu-O material has been prepared using standard solid-state reaction techniques.³ It has a zero-resistance temperature of 90 K, and thus we believe it corresponds to the oxygen-deficient triple-layer perovskite structure of the Koinuma¹ material. X-ray photoelectron spectra of these powders have been obtained on a Kratos ES300 spectrometer. The powders of each oxide have been pressed onto a gold sheet in order to minimize charging. Calibration of the energy scale has been achieved using the C 1s peak of external reference carbon, which is assigned a value of 285.0 eV. Since alkaline earth, transition metal, lanthanide, and actinide oxides react readily with H₂O and CO₂ to form hydroxides and carbonates, spectra have been recorded before and after heating to 400°C for 30 min in the spectrometer.

The superconducting volume fraction has been determined by Koinuma *et al.*¹ as follows. Mixtures of 80 vol % of Y-Ba-Cu-O and 20 vol % of substrate materials are heated at 900°C for 2 h and cooled slowly to 400°C in a furnace at a rate of 1°C/min. The reaction products have been determined by X-ray diffraction (XRD). The relative volume fraction of superconductivity has been estimated from the ac susceptibility at 1 kHz, measured from the change of inductance of the coil which has been wound around the sample tube. The relative volume fraction is determined by dividing the dL/W value, where dL is the change of the coil inductance and W is the sample weight, measured at 4.2 K for a heated sample by that for the sample prior to the heat treatment.

RESULTS AND DISCUSSION

Since an acid-base reaction is usually exothermic, the gradient of the chemical potential which drives the reaction is usually large. Therefore it can be expected, from a thermodynamic point of view, that the interaction between Y-Ba-Cu-O superconducting films and acidic oxides occurs readily. Under ordinary circumstances, the reaction is limited by mass transport to the interface, which is a slow process. However, in the process of heat treatment at high temperature, the superconducting material is in a slight fusion state. Atomic diffusion is enhanced, so that from a dynamics point of view, the speed of the solid phase chemical reaction between Y-Ba-Cu-O and the substrate reaches a measurable level. In the case of Y-Ba-Cu-O thin films on binary oxide substrates, Ba-containing compounds are formed as reaction products. Cheung and Ruckenstein⁵ and Koinuma *et al.*¹ have shown that the reaction of Y-Ba-Cu-O and binary oxide substrates (ZrO₂, Al₂O₃, SiO₂, etc.) results in the formation of BaZrO₃, BaAl₂O₄, Ba₂SiO₄, etc. It is evident that these may be regarded as neutralization prod-

ucts, which are formed when basic Y-Ba-Cu-O reacts with these oxides.

In order to discuss the reactivity quantitatively, it is necessary to select a scale by means of which the relative acidity or basicity of substrate oxides can be properly compared. According to Lewis's definition, a solid acid shows a tendency to accept an electron pair, whereas a solid base tends to donate an electron pair. Acidity or basicity of solids can be determined by chemical analysis or spectroscopic methods. However, different values can be obtained under different sample treatment conditions. Since the Y-Ba-Cu-O-substrate reaction takes place during high-temperature processing, it is more suitable to use an acid-base theory of fused systems in discussing these reactions. Lux⁶ and Flood and Forland⁷ have suggested that the acid-base reaction of fused systems can be expressed by the following chemical equation:



which means that O²⁻ can be regarded as the exchanged species in defining acidity or basicity. Yanagisawa, Watanabe, and Seki⁸ have suggested that the energy of dissociation U for the reaction $\text{MO} \rightleftharpoons \text{M}^{2+} + \text{O}^{2-} + U$ (kcal/mol) is a measure of basicity. Since a base is an O²⁻ donor, the larger the value of U , the easier is the dissociation, and hence the stronger is the basicity of MO. These authors have calculated values for U/mP , where m is the number of cations in the chemical formula of the oxide and P is the coordination number to oxygen, for CaO, MgO, Al₂O₃, and SiO₂. These values are 139, 155, 456, and 777 kcal/mol of oxide, respectively. U/mP can be calculated for any oxide by the use of the Born-Haber cycle, provided that the energy change for the reaction $\text{O}_g^- + e^- \rightleftharpoons \text{O}_g^{2-}$ is known. The energy for this reaction can be estimated by applying the Born-Haber cycle to CaO, MgO, Al₂O₃, and SiO₂ and using the U/mP values of Yanagisawa, Watanabe, and Seki.⁸ A value of 194 ± 6 kcal/mol is obtained. Using thermodynamic data from the *Handbook of Chemistry and Physics*⁹ and the above value, $U/mp = 131, 124, \text{ and } 435$ kcal/mol for SrO, BaO, and ZrO₂, respectively. Figure 1 shows the

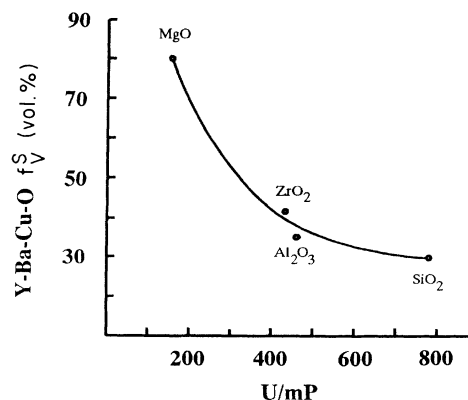


FIG. 1. Plot of relative volume fraction of superconductivity at 4.2 K for mixtures of Y-Ba-Cu-O and substrate materials by 2-h heat treatment at 900°C against dissociation energy of the substrate materials.

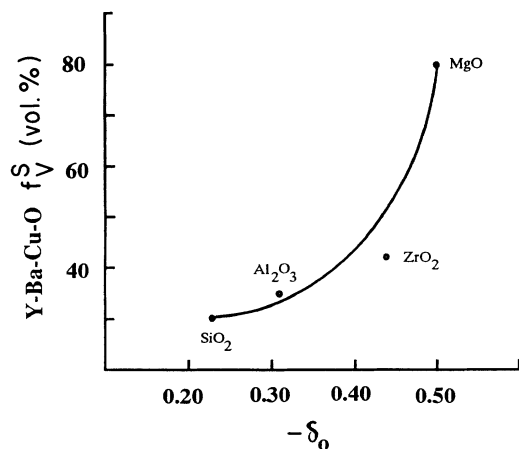


FIG. 2. Plot of relative volume fraction of superconductivity at 4.2 K for mixtures of Y-Ba-Cu-O and substrate materials by 2-h heat treatment at 900 °C against magnitude of partial charge on oxygen.

plot of relative volume fraction of superconductivity at 4.2 K for mixtures of Y-Ba-Cu-O and MgO, ZrO₂, Al₂O₃, or SiO₂ heated for 2 h at 900 °C, abbreviated as f_V^S hereafter, versus U/mP . It shows that the reactivity of Y-Ba-Cu-O with these oxide substrates increases in the order MgO, ZrO₂, Al₂O₃, SiO₂ (correlation coefficient = -0.882), which parallels the increase in acidity. This shows that U/mP is a good measure of reactivity and validates the suitability of an acid-base approach to defining ceramic superconductor-substrate interactions.

Equation (4) implies that acid-base reactions in fused systems can be regarded as electron pair donating-accepting reactions through the medium of oxygen. For an atom, its tendency to donate or accept electrons is closely related to the electron density on the atom. Thus, the partial charge on oxygen, as mediated by the cations, should be a good measure of acid or base strength. Figure 2 shows a plot of f_V^S versus the magnitude of the partial charge on oxygen.¹⁰ It is evident that the magnitude

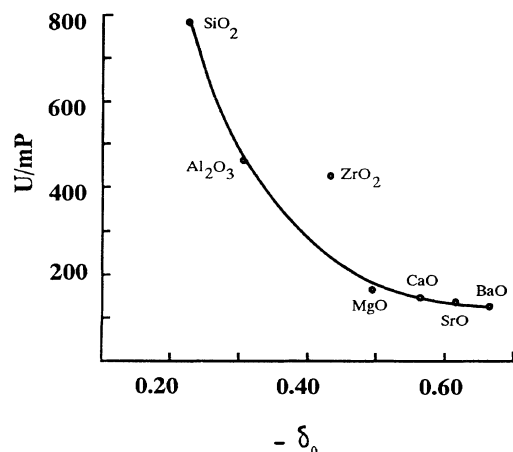


FIG. 3. Relationship between magnitude of partial charge on oxygen and the dissociation energy of various binary oxides.

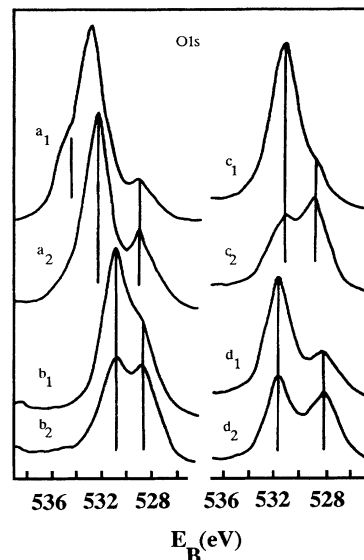


FIG. 4. O 1s XPS spectra of the alkaline earth oxides before and after heating in the spectrometer at 400 °C. a_1, a_2 , MgO; b_1, b_2 , CaO; c_1, c_2 , SrO; d_1, d_2 , BaO.

of the partial charge on oxygen is correlated with the Y-Ba-Cu-O-substrate reactivity, and that the reactivity decreases with increasing electron density (as reflected by $-\delta_0$) on oxygen. Thus U/mP and $-\delta_0$ should be highly correlated, and indeed this is the case (correlation coefficient = -0.929), as shown in Figure 3.

According to the electrostatic potential model,¹¹ the Fermi referenced binding energy of an electron on an atom or ion in a solid depends on the energy required to eject the electron from the free atom or ion; the chemical shift, which is directly related to the charge on the atom or ion; and the lattice potential of the solid and the extra-atomic relaxation energy. For oxygen in oxides, when all of the contributions except the chemical shift are similar, the O 1s binding energy will be highly correlated with the magnitude of the partial charge on oxygen. In such a case, the O 1s binding energy is a potential measure of acidity or basicity. Since basic oxides react readily with H₂O and CO₂, multiple peaks are always observed in the X-ray photoelectron spectroscopy (XPS) spectra of such samples, when they have not been etched

TABLE I. O 1s binding energies (eV) of Y-Ba-Cu-O superconductor and various binary oxides.

Oxide	Lattice oxygen	Contaminant oxygen
Y-Ba-Cu-O	527.0–528.5	531.0
BaO	528.1	531.4
SrO	528.6	531.0
CaO	528.8	530.7
MgO	529.0	532.1
ZrO ₂	530.1	
Al ₂ O ₃	531.6	
SiO ₂	532.8	

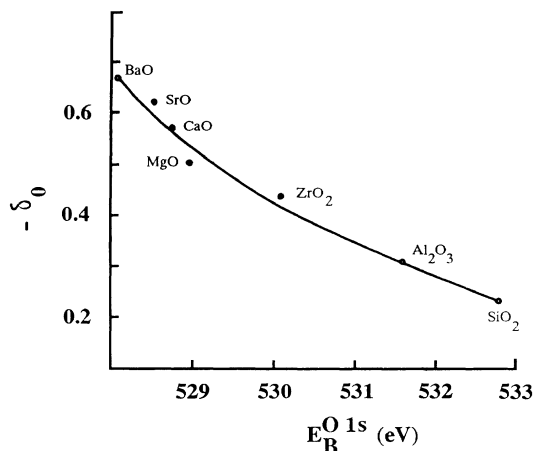


FIG. 5. Correlation between magnitude of partial charge on oxygen and the lattice O 1s binding energy of various binary oxides.

or extensively heated in vacuum at temperature greater than or equal to 400°C. This is illustrated for MgO, CaO, SrO, and BaO in Fig. 4, a_1-d_1 . The O 1s binding energy of interest is that due to lattice oxygen. It is not necessary to completely remove contaminant oxygen in order to determine unequivocally the lattice oxygen binding energy. It is sufficient to treat the samples to remove enough contaminants so that changes in the relative intensities can be used. Heating to 400°C for 30 min suffices for this purpose, as shown in Fig. 4, a_2-d_2 . It is clear that the lower binding energy peak increases after this treatment, and thus it can be assigned to the lattice oxygen. The O 1s binding energy data are summarized in Table I. The O 1s binding energies for lattice oxygen of MgO, CaO, and SrO, as determined in the present work, are lower than those reported in the literature. The O 1s binding energy of MgO has been reported to be 531.0 eV

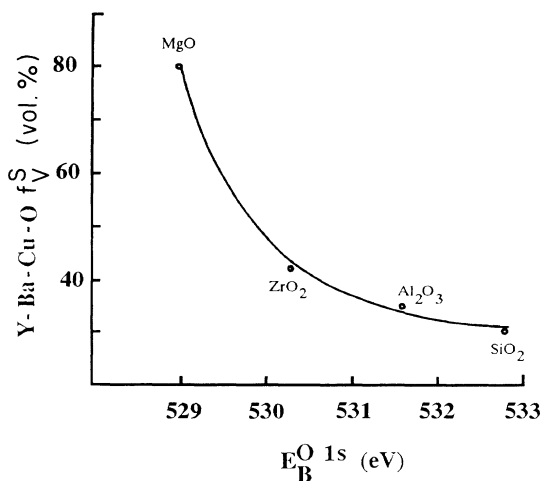


FIG. 6. Plot of relative volume fraction of superconductivity at 4.2 K for mixtures of Y-Ba-Cu-O and various substrate materials by 2-h heat treatment at 900°C against the O 1s binding energy of the substrate material.

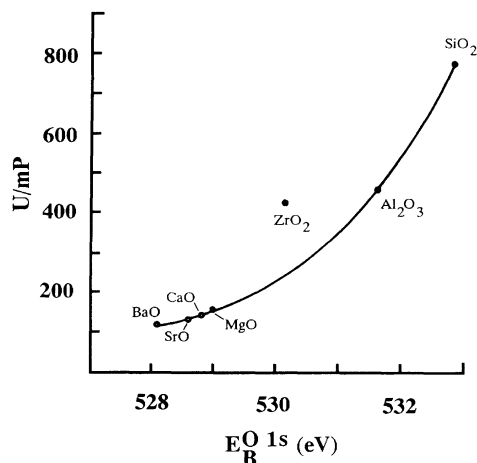


FIG. 7. Relationship between the lattice O 1s binding energy and the dissociation energy of the binary oxides.

(Ref. 12) and 531.2 eV (Ref. 13) and that for CaO to be 529.9 eV.¹⁴ For SrO, values of 530.3 eV (Ref. 14) and 530.1 eV (Ref. 15) have been reported. Young and Otawaga¹⁵ did observe an O 1s peak at 528.3–528.5 eV for scraped Sr plate. This they attributed to adsorbed O⁻, in agreement with the results of Barteau and Madix.¹⁶ It is possible that the higher binding energies observed by others on the powders may be attributed to surface contamination, since the samples were neither etched nor heated to elevated temperatures. Stinespring and Cook¹⁷ have reported that the O 1s peak of CaO single crystals prior to ion etching is mainly from surface contaminants (e.g., CaCO₃) with a binding energy of 531.8 eV; after ion etching, the O 1s peak is mainly from lattice oxygen with a binding energy of 528.8 eV, the same as observed in this study. Although ion etching is a destructive process, so that the “oxide” at the near surface region may be quite different from lattice oxide, in our case the samples were heated at a temperature which only provides sufficient thermal energy to decompose hydroxides and carbonates. By contrast, the O 1s binding energy of Y-Ba-Cu-O as determined in the present work is higher than the accepted value for clean, high-quality crystals, 528.0 eV.¹⁸ This higher value is not unexpected, since the Y-Ba-Cu-O material is oxygen deficient. Some of the lack of agreement

TABLE II. Summary of data used in this paper.

Oxide	O 1s E_B (eV)	$-\delta_0^a$	U/mP (kcal/mol)	Y-Ba-Cu-O ^b at 900°C
BaO	528.1	0.67	124	
SrO	528.6	0.62	131	
CaO	528.8	0.57	139 ^c	
MgO	529.0	0.50	155 ^c	80
ZrO ₂	530.1	0.44	435	42
Al ₂ O ₃	531.6	0.31	456 ^c	35
SiO ₂	532.8	0.23	777 ^c	30

^aReference 10.

^bReference 1.

^cReference 8.

TABLE III. Patterns of deviation of ZrO_2 from the curves of Figs. 1–7.

Figure	δ_0 in error	O 1s in error	U/mP in error	Observed
1	On	On	Off	On
2	Off	On	On	Off
3	Off	On	Off	Off
5	Off	Off	On	On
6	On	Off	On	On
7	On	Off	Off	Off

may also be due to differences in referencing. The C 1s peak of the spectra of Ref. 18 shows a maximum at 284.0 eV, while we have taken C 1s at 285.0 eV as the reference. It is important that all samples be referenced in the same way, if trends are to be analyzed. Differences in referencing will only result in static shifting of the correlation plots, leaving the trends observed invariant.

Figure 5 shows a plot of the magnitude of partial charge on oxygen as a function of O 1s binding energy. These two parameters are very highly correlated (correlation coefficient = -0.982), showing that contributions to the O 1s binding energy other than the chemical shift are similar in these oxides. Thus, the O 1s lattice binding energy is a good measure of reactivity, as shown in Fig. 6 (correlation coefficient = -0.875). This shows that the oxide substrate material with the lower lattice O 1s binding energy (stronger basicity) is relatively stable to chemical reactions with Y-Ba-Cu-O. From Table I, one can also see that the lattice O 1s binding energy for Y-Ba-Cu-O is the same as that of MgO, reflecting that Y-Ba-Cu-O is similar to MgO in basicity. Therefore MgO is the most inert oxide substrate, of those studied, reacting only slightly with Y-Ba-Cu-O during heat treatment processing.^{1,19,20} It is evident that the lattice O 1s binding energy may represent a quick way of screening potential oxide substrate candidates. The correlation between the lattice O 1s binding energy and U/mP (Fig. 7, correlation coefficient = 0.965) is even stronger than that between the lattice O 1s binding energy and $-\delta_0$. All of the data used to make the graphs and to calculate the correlation coefficients are summarized in Table II.

CONCLUSIONS

One cannot help but notice that the point for ZrO_2 falls well off the line in several of the figures. Table III shows the on or off pattern expected if $-\delta_0$ is in error, if the lattice O 1s binding energy is in error, or if U/mP is in error. The observed pattern shows that the fault does not lie with the lattice O 1s binding energy, but it fits neither the pattern for faulty $-\delta_0$ nor for faulty U/mP . The calculation of U/mP ($m = 1$, $P = 6$, crystal structure = α phase) has been checked and rechecked. No error can be found. This suggests that the reactivity curve, using U/mP as the measure, for binary transition-element oxides may not lie along the same curve as the oxides of the representative elements. More experiments using transition-element oxides will need to be performed before this possibility can be addressed.

In general, all three of the parameters are useful measures of reactivity. Of these, the lattice O 1s binding energy may be the most useful for oxide supports, for the following reasons. It is easy to measure the lattice O 1s binding energy for complex oxides (ternary, etc.), while it is not clear how one would calculate U/mP for such cases. Potentially, the lattice O 1s binding energy may give points which all lie along a universal curve. Values for $-\delta_0$ must be calculated, and they are very dependent on both the method used and its parametrization. It certainly seems worthwhile to study these measures more extensively, as they may possibly prove useful as design tools in the application of thin-film ceramic superconductors.

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