Carbonatization of YBa$_2$Cu$_3$O$_{6+x}$


Department of Chemistry, University of Oslo, Blindern, N-0315 Oslo 3, Norway


YBa$_2$Cu$_3$O$_{6+x}$ reacts with CO$_2$ at a significant rate at temperatures above ~400°C. The stability of YBa$_2$Cu$_3$O$_{6+x}$ towards reaction with CO$_2$ in CO$_2$ + O$_2$ mixtures ($p_{O_2} = 1.00$ atm) has been established as a function of CO$_2$ partial pressure and temperature. Below 730±10°C the reaction products are BaCO$_3$, Y$_2$O$_3$ and CuO. Above this temperature the products are BaCO$_3$, Y$_2$Cu$_2$O$_3$ and CuO. Thermodynamic parameters for the two reactions have been evaluated for $x = 0.5$.

The recently discovered class of high $T_c$ superconducting oxides has properties which open up for many applications. The first efforts to explore the properties of these compounds were naturally concentrated on the characterization of phase diagrams and crystal structures, as well as on the systematic mapping of key physical parameters. However, in order to evaluate their potential use in practical superconducting devices, properties connected with grain boundaries, surfaces and, in particular, chemical reactivity towards environmental components become of utmost importance.

The superconducting YBa$_2$Cu$_3$O$_{6.5}$ phase (in the following most conveniently expressed as YBa$_2$Cu$_3$O$_{6+x}$, with $0 \leq x \leq 1$) is reported to be degraded by water.$^{1,2}$ Upon heating or when exposed to lower partial pressures of oxygen, the oxygen content is reduced from a maximum of seven to a minimum of six atoms per formula unit.$^{4,5}$ Reactions with gaseous species during the syntheses may be important and it has, for instance, been reported$^{10}$ that in interaction with N$_2$ at elevated temperature some nitrogen can replace oxygen in YBa$_2$Cu$_3$O$_{6+x}$. Unfortunately, many studies on the new oxide superconductors have been performed on phase-impure samples. The latter problem derives partly from a lack of knowledge of the phase diagram and inappropriate preparative procedures.

The metal constituents of YBa$_2$Cu$_3$O$_{6+x}$ exhibit a relatively high average electropositive character, and the interdependent high basicity$^{11}$ of the constituent oxides (in particular BaO) suggests that a detectable reaction between the quaternary oxide and CO$_2$ could proceed even at relatively low CO$_2$ partial pressures and high temperatures. In order to make practical use of the superconducting phases it is important to clarify this aspect.

The $p, T$ equilibrium for decomposition of carbonates can be established using static$^{12}$ or dynamic$^{13}$ methods. The former procedure is based on direct measurements of the CO$_2$ decomposition pressure at fixed temperatures. In the dynamic procedure, on the other hand, one of the thermodynamic variables (e.g. $T$) is set at a value around the expected equilibrium value and the response of the reaction system is registered while monitoring the second variable (e.g. $p_{CO_2}$).

The present paper reports on dynamic thermogravimetric measurements made under conditions of varying temperature and CO$_2$ partial pressure. The apparatus and procedures employed are similar to those in the cyclic thermogravimetric method reported recently.$^{14}$ The method has the great advantage of being sensitive to even small degrees of carbonatization of the oxide samples.

Materials and methods

Preparation. The quaternary oxide was prepared from CuO, BaCO$_3$ (both reagent grade; Merck) and Y$_2$O$_3$ (99.999%); Megen, Norway). A stoichiometric mixture of the dried and analyzed
components was homogenized to a slurry by milling under acetone in a Fritsch Pulverisette laboratory grinder for 12 h. After firing at 900°C in air for 24 h, the product was re-homogenized twice by milling under carbon tetrachloride and re-annealed under similar conditions in the form of sieved powder in a corundum boat. The final sequence comprised a 24 h annealing in air at 400°C.

Chemical analysis. The copper and oxygen contents were determined iodometrically using 0.1 M Na₂S₂O₃ (Titrisol; Merck) standardized against KIO₃. Approximately 0.2 g of an accurately weighed, pulverized sample was dissolved in 1 M HCl in an Erlenmeyer flask, the solution heated to dryness and the residue redissolved in acidified water. The iodine released after adding ~1 g of KI in 20 ml of water was titrated, thus providing a measure of the copper content. The total oxidative power towards I⁻ was determined separately. The iodine (to be titrated) was then released during reaction of a suspension of the (previously weighed) sample in 20 ml of 5% KI to which 10 ml of 1 M HCl was slowly added during stirring (the Erlenmeyer flask being filled with argon in advance). No analyses for yttrium or barium were performed since all samples used in this study were shown by X-ray diffraction to be single-phase; this fixes the contents of these elements relative to copper according to the stoichiometry of YBa₂Cu₃O₆+x.

X-Ray diffraction. The homogeneity of all samples was checked at room temperature by powder X-ray diffraction using a Guinier Hägg camera (CuKα, and CrKα radiation, Si as internal standard). Corresponding high-temperature data were obtained between 20 and 1000°C in a Guinier Simon camera. Unit cell dimensions were derived by least-squares refinements.¹⁵

Thermogravimetric measurements. The sample material was pulverized, and ~1.4 g of powder was weighed into a pre-annealed alumina crucible.

A Sartorius model 4410 balance was used, with platinum wires suspended on both balance arms. One wire held the sample crucible inside a mullite tube in the hot zone of a tube furnace. The other wire held an identical counter-weight crucible inside a glass tube at room temperature. The tubes and the balance were part of a gas-tight system through which gas mixtures could be fed.

The precision of the balance itself is 1 μg, but the use of elevated temperatures and gas flow past the sample introduced fluctuations that reduced the precision to about 10 μg. The long-term reproducibility was 40 μg.

The temperature was controlled and monitored by a Pt/Pt + 10 % Rh thermocouple located close to the sample crucible. The thermocouple reading was checked against the true temperature in the crucible as follows: CaCO₃ (p.a.) powder was used as sample in ~1.00 atm of CO₂. Increasing the temperature the weight of the sample started to decrease at 898°C. On decreasing the temperature the weight increased at 897°C. Thus, the apparent decomposition temperature of CaCO₃ under ~1.00 atm of CO₂ was assumed to be 897–898°C. The decomposition of CaCO₃ has recently been carefully examined by a similar method, and a decomposition temperature of 897°C at 1.00 atm of CO₂ was found.¹⁴ These results confirm that the thermocouple readings corresponded within ±1°C to the actual temperature at the crucible position.

Control of atmosphere. Controlled partial pressures of CO₂ were obtained by mixing CO₂ or air with oxygen in ratios of between 1 and 5000 using precision flowmeters. In this series of experiments the oxygen partial pressure was kept constant (~1.00 atm). The CO₂ content in the compressed air cylinders was reported to be 300 ppm. The oxygen used contained typically 14 ppm of CH₄ (which is assumed to react to give CO₂ in the furnace), and the CO₂ content in O₂ is therefore estimated to be 14 ppm. CO₂ contents above 200 ppm were produced by mixing CO₂ with O₂. CO₂ contents between 14 and 100 ppm were obtained by mixing air with O₂.

Atmospheres with variable O₂ partial pressures were established in the same system by mixing oxygen with argon.

The gas mixtures were dried with P₂O₅. The total pressure in the furnace was around 1.00 atm, the exact value being monitored with a manometric pressure gauge.

Thermogravimetric procedures. The stability of the quaternary oxide with regard to carbonate formation was studied as follows: At each partial pressure of CO₂ the temperature was increased...
or decreased in steps, and the change in the sample weight was recorded. A weight increase is assumed to correspond to carbonate formation, and a weight decrease to carbonate decomposition (i.e. the quaternary oxide is stable). The equilibrium was found by averaging the two closest points representing weight increase and decrease, or as points where no weight change could be observed. The determination of the equilibrium temperature was performed with a precision ranging from about 1°C above 800°C to about 10°C below 700°C.

When significant amounts of CO₂ or air were added to the oxygen, minor weight changes occurred due to the corresponding changes in the oxygen partial pressure. These changes could, however, be distinguished from those associated with the carbonate reaction by their different kinetic behaviour: The reaction with O₂ is fast and the sample weight rapidly reaches a new equilibrium value, while the CO₂ reaction is slow and the sample weight continues to change for extended periods.

The determination of the changes in oxygen content of the sample for each set of temperature and oxygen partial pressure conditions was done using standard thermobalance calculations based on relative weight readings and on the weight and oxygen content of the initial sample. Corrections were made for the buoyancy of both crucibles (with contents), taking into account temperature, composition of the gas mixture and total pressure. Loss of H₂O and CO₂ recorded during the very first heating cycle was used to correct the initial weight of the sample and the initial thermobalance weight reading.

**Results and discussion**

(i) **Structural properties.** Powder X-ray diffraction analysis confirmed that the YBa₂Cu₃O₆₊ₓ sample used in this study was single-phase with unit cell dimensions \( a = 382.04 \pm 0.03, b = 388.82 \pm 0.03 \) and \( c = 1168.47 \pm 0.1 \) pm. From iodometric titration the oxygen content was established to be \( 6.93 \pm 0.02 \) per formula unit. The unit cell dimensions and particularly the degree of orthorhombic deformation agree with recently established correlations between structural characteristics and oxygen content.

Within the orthorhombic YBa₂Cu₃O₆₊ₓ-type variant of the perovskite atomic arrangement, the easily removable oxygen atoms are (at low temperature) confined to one particular crystallographic site, viz. 0.1/2.0.¹⁶⁻¹⁹ High temperature powder X-ray diffraction studies (Guinier Simon technique) in air showed vanishing orthorhombic distortion at 690±20°C.²⁰ The “driving force” of the orthorhombic to tetragonal “phase transition” is redistribution of oxygen atoms over more sites – a process which takes place parallel with removal of oxygen from the structure. **Formally,** the redox process can be described as

\[
\text{Cu}_{\text{lattice}}^{III} + \text{O}_{\text{lattice}}^{II} \rightarrow \text{Cu}_{\text{lattice}}^{II} + \text{Cu} + 1/2 \text{O}_2(g). \tag{1}
\]

(ii) **High-temperature reaction with CO₂.** Carbonization of YBa₂Cu₃O₆₊ₓ, i.e. reaction with CO₂ to form carbonates, proceeds with measurable rates at temperatures above 400°C. However, different reaction products are formed depending on the temperature. Below 730±10°C the oxides of yttrium and copper are formed together with barium carbonate:

\[
\begin{align*}
\text{YBa}_2\text{Cu}_3\text{O}_{6+x}(s) + 2 \text{CO}_2(g) & \rightarrow \\
2 \text{BaCO}_3(s) + 1/2 \text{Y}_2\text{O}_3(s) + 3 \text{CuO}(s) + (2x - 1)/4 \text{O}_2(g) & \tag{2}
\end{align*}
\]

Above 730±10°C, the turquoise blue Y₂Cu₂O₅ is a reaction product:

\[
\begin{align*}
\text{YBa}_2\text{Cu}_3\text{O}_{6+x}(s) + 2 \text{CO}_2(g) & \rightarrow \\
2 \text{BaCO}_3(s) + 1/2 \text{Y}_2\text{Cu}_2\text{O}_4(s) + 3 \text{CuO}(s) + (2x - 1)/4 \text{O}_2(g) & \tag{3}
\end{align*}
\]

![Fig. 1. Temperature dependence of oxygen content (x) of YBa₂Cu₃O₆₊ₓ at 1.00 atm of O₂.](image)
The reactions proceed for certain combinations of the variables of \( x, p_{CO_2} \) and \( T \) [see section (iv)]. In order to characterize the different reaction products, prolonged reaction times at 600 and 850°C, respectively, followed by rapid cooling of the sample in the reaction atmosphere were adopted. The various phases were identified on the basis of powder X-ray diffraction diagrams, and the evaluated unit cell dimensions corresponded well with those found for the pure products.30 Thus, mutual solid solubility of the reaction products was negligible.

(iii) High temperature reaction with \( O_2 \) in mixture with \( CO_2 \). Some investigators have claimed that \( YBa_2Cu_3O_{6+x} \) is able to accommodate nitrogen in oxygen sites.10 The present thermogravimetric measurements in \( O_2/Ar \) and \( O_2/N_2 \) (20/80 \( v/v \)) mixtures at 600°C gave no support for such a conclusion.

The oxygen content of \( YBa_2Cu_3O_{6+x} \) is a function of both temperature and oxygen partial pressure. For \( x = 0.50 \) the oxidation state of copper is equal in the reactants and the products, and no oxygen is evolved or consumed during the carbonatization [eqns. (2) and (3)]. However, in general the carbonatization involves either release (\( x > 0.5 \)) or uptake (\( x < 0.5 \)) of oxygen. Thus, a quantitative treatment of the reactions with \( CO_2 \) will require knowledge of the equilibrium between \( YBa_2Cu_3O_{6+x} \) and oxygen.

(iv) \( x, p, T \) equilibrium in \( O_2 \). The oxygen content or the non-stoichiometry of \( YBa_2Cu_3O_{6+x} \) varies strongly with temperature, as illustrated in Fig. 1 for a constant oxygen partial pressure of 1.00 atm. Under such conditions the maximum oxygen content corresponds to \( x = 0.955 \), which is in agreement with earlier reported equilibrium data.1,8 The \( x \) versus \( 1/T \) relationship is essentially linear in the temperature range 600–900°C, and can be parameterized as:

\[
x = A/T + B
\]

where \( A \) and \( B \) have values of 1390 K and \(-0.83 \), respectively.

The oxygen partial pressure in equilibrium with \( YBa_2Cu_3O_{6.5} \) is plotted versus reciprocal temperature in Fig. 2 for the temperature interval 520–780°C. The relationship can empirically be described as:

\[
\log p_{O_2} = C/T + D
\]

with \( C = -8350 \) K and \( D = 8.0 \) for \( p_{O_2} \) specified in atm. According to Fig. 2, \( YBa_2Cu_3O_{6.5} \) is stable at \(-775 \)°C in pure oxygen (1.00 atm) and at \(-690 \)°C in air. These temperatures coincide with those for the orthorhombic to tetragonal structural transition. Independent studies21–24 have found the latter structural transition to occur for \( x = 0.5 \) in different atmospheres. The \( p_{O_2} \) versus
1/T relationship for YBa$_2$Cu$_3$O$_{6.5}$ also corresponds, to a good approximation, to the variation of the distortion temperature with the oxygen pressure.

(v) p,T equilibrium for reaction with CO$_2$. The results of the reaction studies on YBa$_2$Cu$_3$O$_{6.5}$ in CO$_2$-containing atmospheres are summarized in the log $p_{CO_2}$ versus 1/T plot in Fig. 3. The fully-drawn line and the shaded strip in Fig. 3 separate the stability regions of reactants and products. The quaternary oxide is thus stable at higher $T$ and lower $p_{CO_2}$. Consistent with the observation of two different sets of reaction products, the equilibrium boundary shows a kink or jump at around 730°C.

At lower temperature and reduced $p_{CO_2}$, any weight changes become increasingly difficult to register. This is probably due to slower diffusion of carbon dioxide and/or metal atoms in the sample, and to the low CO$_2$ content of the atmosphere itself. The measurements at the lowest CO$_2$ partial pressures are furthermore burdened by the rather uncertain estimate of the content of carbonaceous impurities in the oxygen gas. Additional sources of uncertainty concerning these conditions may originate from competing reactions with the inevitable trace amounts of H$_2$O present in the gas mixtures, and the fact that formation of YBa$_2$Cu$_3$O$_{6.5}$ from the oxide constituents is slow at the temperatures concerned. Thus, while the equilibrium line for reaction according to eqn. (3) can be well established, the equilibrium for eqn. (2) cannot be determined with the same accuracy.

At 300°C in air no carbonization could be detected (although thermodynamically it should take place, Fig. 3), at 400°C the reaction proceeds at a rate of ~0.006% per hour, while at 500 and 600°C the corresponding rates amount to 0.026 and 0.047% per hour, respectively. The reaction rate at 600°C may be limited by the rate of supply of CO$_2$.

The equilibrium diagram in Fig. 3 puts restrictions on the procedures for the synthesis of high-purity YBa$_2$Cu$_3$O$_{6.5}$. The compound can only be successfully prepared from BaCO$_3$ and oxides under conditions to the left of the equilibrium boundary in Fig. 3. The CO$_2$ content of air (300 ppm) and the content of carbonaceous gases in commercial, pressurized oxygen (~10 ppm) restrict the lowest temperatures for preparation to 700 and 650°C, respectively. If crucibles with poor circulation of air/oxygen near the sample are used, it may be difficult to obtain a carbonate-free product even at significantly higher temperatures.

The superconductivity of YBa$_2$Cu$_3$O$_{6.5}$ is highly dependent on $x$, and the highest $T_C$ is obtained for $x = 1.0$. Therefore, after the firing at some 900°C the samples are generally annealed at 300–400°C in air or oxygen in order to ensure a high oxygen content. The present results show that such a treatment may lead to partial carbonatization of the sample, impurities probably accumulating at grain boundaries and surfaces. This problem can be avoided by using CO$_2$-free gases. Moreover, the annealing can be carried out at 250–300°C. At these temperatures the equilibration with respect to oxygen is reasonably fast, whereas the rate of carbonization is practically zero.

Included in Fig. 3 are the equilibria between oxides and carbonates of calcium, strontium and barium. It is seen that the properties of YBa$_2$Cu$_3$O$_{6.5}$ are comparable to those of SrO.

(vi) Thermodynamic considerations. The equilibrium data (Fig. 3) for the carbonization reactions [eqns. (2) and (3)] can be expressed as standard enthalpy and entropy changes. However, the equilibrium CO$_2$ partial pressure refers to the YBa$_2$Cu$_3$O$_{6.5}$ phase where $x$ varies with temperature at constant $p_{0_2} = 1.00$ atm. Thus, the log $p_{CO_2}$ versus 1/T relationship will, in principle, not be defined by a straight line. It is hence inconvenient for our purposes to define the reference state of the quaternary oxide as the stable composition at a given temperature and $p_{0_2} = 1.00$ atm. Therefore, all calculations refer to the composition YBa$_2$Cu$_3$O$_{6.5}$, thus eliminating the internal redox reaction [eqn. (1)].

In the experiments, $p_{0_2}$ was kept close to 1.00 atm, and in the temperature range in question, i.e. 650–930°C, the compositional variable $x$ is fairly close to 0.5. This implies that the equilibrium expression for the chemical reactions [eqns. (2) and (3)] can be simplified according to:

$$K = p_{CO_2}^{0.14} \cdot p_{O_2}^2 \approx p_{CO_2}^2.$$

In order to refer changes in the standard Gibbs energy, $\Delta G^\circ$, enthalpy, $\Delta H^\circ$, and entropy, $\Delta S^\circ$, to the reference composition $x = 0.5$, corrections due to the internal oxygen equilibrium reaction:
Table 1. Standard enthalpy and entropy changes for carbonatization of \(\text{YBa}_2\text{Cu}_3\text{O}_{6+x}\).

<table>
<thead>
<tr>
<th></th>
<th>Temperature</th>
<th>(\Delta H)(^{\circ})kJ mol(^{-1})</th>
<th>(\Delta S)(^{\circ})J mol(^{-1}) K(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2)*</td>
<td>650–730</td>
<td>(-680\pm270)</td>
<td>(-570\pm280)</td>
</tr>
<tr>
<td>(3)</td>
<td>730–930</td>
<td>(-346\pm15)</td>
<td>(-229\pm14)</td>
</tr>
</tbody>
</table>

*See comments about uncertainty in section (v).

\[\text{YBa}_2\text{Cu}_3\text{O}_{6+4}(s) \rightarrow \text{YBa}_2\text{Cu}_3\text{O}_{6+5}(s) + (2x-1)/4 \text{O}_2(g)\]  

(7)

must be made. Thus, the change in standard Gibbs energy for the reactions (2) and (3) with \(x=0.5\) is:

\[\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = 2RT \cdot \ln p_{\text{CO}_2} - \Delta G^{\circ}_{\text{redox}} \]  

(8)

where

\[\Delta G^{\circ}_{\text{redox}} = (1-2x)/4 \cdot RT \cdot \ln p_{\text{O}_2}.\]  

(9)

On introduction of the empirically deduced relations, eqns. (4) and (5) for the temperature dependences of \(x\) and \(\log p_{\text{O}_2}\), \(\Delta G^{\circ}_{\text{redox}}\) for the chemical reaction (7) becomes:

\[\Delta G^{\circ}_{\text{redox}} = \alpha T + \beta + \gamma T \]  

(10)

where \(\alpha = 0.102\ \text{kJ K}^{-1}\ \text{mol}^{-1}\), \(\beta = -212.7\ \text{kJ mol}^{-1}\) and \(\gamma = 111.2 \cdot 10^3\ \text{kJ K}^{-1}\ \text{mol}^{-1}\) over the temperature range 600–900°C. The derived values of \(\Delta H^{\circ}\) and \(\Delta S^{\circ}\) for the reactions in eqns. (2) and (3) with \(x=0.5\) are given in Table 1. On the basis of the thermodynamic data for the reaction components [eqn. (2); assuming \(\Delta C_p = 0\) for the reaction] listed in the JANAF tables,\(^{27}\) the standard enthalpy of formation for \(\text{YBa}_2\text{Cu}_3\text{O}_{6.5}\) is \(\Delta H^{\circ}_{\text{f},298} = -2400\pm270\ \text{kJ mol}^{-1}\) (no data are available for \(\text{Y}_2\text{Cu}_3\text{O}_5\)).

On comparing the deduced \(\Delta G^{\circ}\) values for the oxygen shift reaction [eqn. (7)] and the carbonatization reactions [eqns. (2) and (3)] at various temperatures, it is seen that \(\Delta G^{\circ}\) for the former reaction is comparable in magnitude with the uncertainty in \(\Delta G^{\circ}\) for the latter. This feature is mainly due to the uncertainty in the control and measurement of \(p_{\text{CO}_2}\).

The tendency of the \(\text{YBa}_2\text{Cu}_3\text{O}_{6+x}\) superconductor material towards carbonatization is largely due to the large content of the alkaline earth element. Thus, a similar behaviour is also expected for the rare earth-substituted analogues \(\text{REBa}_2\text{Cu}_3\text{O}_{6+x}\). In all probability, \(\text{YSr}_2\text{Cu}_3\text{O}_{6+x}\), if it exists, is less susceptible to carbonatization due to the reduced stability of \(\text{SrCO}_3\).

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References


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