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KINETIC STUDY ON THE REACTION OF
$YBa_2Cu_3O_y$ POWDER WITH WATER

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The reaction of superconducting $YBa_2Cu_3O_y$ powder with water is studied kinetically. The initial rate law is found as $R_o = k[S]_o^a [H_3O^+]_o^b$ where $[S]_o$ is the initial surface area of the solid, a and b is found to be 0.94 ± 0.02 and 0.318 ± 0.002, respectively. For 100.7 mg powder with a mean radius of 0.0265 mm at pH 7.00 and 298 K, R_o is 2.21×10^{-4} mol $\cdot$ min^{-1}. Using $a = 1$ and $b = 0.3$, the rate constant, k, obtained at 283, 298 and 313 K is 0.64, 1.84 and 4.91×10^{-3} mol $\cdot$ min$^{-1} \cdot$ cm$^{-2} \cdot$ M$^{-0.3}$, respectively. The activation energy is 50.0 kJ $\cdot$ mol^{-1} and pre-exponential factor is 1.09×10^6 mol $\cdot$ min$^{-1} \cdot$ cm$^{-2} \cdot$ M$^{-0.3}$, as calculated from the Arrhenius equation.

Keywords: $YBa_2Cu_3O_y$; superconductors; kinetics; activation energy.

1. Introduction

Since the discovery of high temperature superconductor with a T_c higher than the boiling point of nitrogen in early 1987 by Wu *et al.*[1] wide applications of super-conductors in our daily life become foreseeable. However, high-T_c superconducting cuprates containing alkaline earth cations, such as $YBa_2Cu_3O_{7-\delta}$ (Y-123, $T_c = 93$ K),[2] $(Bi_{2-x}Pb_x)Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi-2223, $T_c = 110$ K),[3] $Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$ (Tl-2223, $T_c = 125$ K),[4] $HgBa_2Ca_2Cu_3O_{8+\delta}$ ($T_c = 133$ K)[5] and $(Sr_{0.7}Ca_{0.3})_{0.9}CuO_2$ ($T_c = 110$ K),[6] are not stable in water or humid vapor.[7,8] When they are in contact with water, the constituent alkaline earth cation gradually dissolves and the pH of the solution is increased.[8−15] Mass equation of Y-123 in water is[16,17]

$$YBa_2Cu_3O_7 + 1.5\ H_2O$$
$$\rightarrow 2.5\ CuO + 1.5\ Ba^{2+} + 3\ OH^- + 0.5\ Y_2BaCuO_5 + 0.25\ O_2 \,. \quad (1)$$
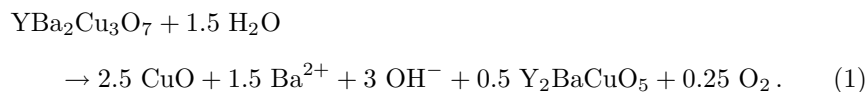
Basicity of barium oxide is the highest among the common alkaline earth oxides. As a result, the deteriorating rate of Y-123 in water is quite high compared with other non-barium containing cuprate superconductors, such as Bi-2223.[12,18,19]

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Although Y-123 is greatly degraded by water and humid air,[9,20] this effect should not preclude its practical application since it is possible to protect Y-123 by coating of silver or glass.[21−24] Although most of the literature reports are focusing on the reaction of high-T_c superconductors with water or vapor qualitatively,[11,16,17] we have investigated the reaction of Bi-2223 with water kinetically.[14,15] It is found that the rate law is first order dependent on the surface area of the powder sample, and the reaction rate is greatly reduced at high pH.[14,15] Since Y-123 is the most widely studied high-T_c superconductor, and its application in the large or small-scale device is under developed, it is important to have kinetic data about the reaction of Y-123 with water. In this paper, the reaction of Y-123 with water is investigated kinetically and the results are compared with those obtained for Bi-2223.

2. Experimental

Y-123 powder obtained from Materials Research Laboratory, Industrial Technology Research Institute in Taiwan, was re-sintered and re-annealed before the reaction with water. Crystalline phase was examined by a Mac Science MXP3 X-ray diffractometer. T_c was obtained from a resistivity temperature curve, in which temperature was measured by a silicon diode sensor near the sample. In the kinetic study, the powder sample was sieved to control the surface area. Its radius is calculated according to the average openings on the sieves to catch the sample. Approximately 50–200 mg of Y-123 powder was used for each experimental condition. Surface area of the powder was calculated from the formula weight, unit cell parameters and the average radius. Reaction vessel was jacketed and circulated with constant temperature water from a circulating bath. Reaction was done in a close system to avoid the interference of the CO_2 in ambient. In order to keep the activity coefficient of the ions at constant during the reaction, all the solutions employed in this study contain 0.100 M $NaNO_3$. Standardized $HCl_{(aq)}$ with a concentration ea. 0.01 N is filled inside a burette controlled by a Radiometer autotitrator. Acid was automatically added into the reaction solution to keep the pH of the reaction at constant. Volume of the acid added with respect to the reaction time was recorded for calculating the initial rate and the reaction order according to the rate law. Activation energy (E_a) and pre-exponential factor (A) of the reaction at different temperature are calculated according to the Arrhenius equation.[25]

3. Results and Discussion

Superconducting transition temperature, $T_{c(\text{onset})}$, $T_{c(\text{zero})}$ and $\Delta T_{c(10–90\%)}$ of Y-123 is found as 93, 92 and 0.7 K, respectively. It is comparable to the literature report.[26] According to the chemical Eq. (1), the rate equation of Y-123 in water is written as follows:

$$R = -d[\text{Y} - 123]/dt = d[\text{Ba}^{2+}]/1.5\,dt = d[\text{OH}^-]/3\,dt$$

$$= d[\text{H}_3\text{O}^+]/3\,dt = k[\text{Y} - 123]^a[\text{H}_3\text{O}^+]^b = k[S]^a[\text{H}_3\text{O}^+]^b\,. \tag{2}$$

The amount of OH$^-$ ion produced in the reaction is the same as the amount of H$_3$O$^+$ added into the solution when pH is kept constant. Thus,

$$d[\text{OH}^-]/3\,dt = d[\text{H}_3\text{O}^+]/3\,dt\,.$$

Because Y-123 is not soluble in water, no concentration is available for [Y-123]. However, its reaction rate should be dependent on the surface area, S, of the Y-123 solid. Thus, [Y-123] is replaced by [S] in the rate law so that particle size becomes an important parameter for the reaction rate studies. Surface area of the powder is calculated from the formula weight, unit cell parameters and the average radius. If there are micro-porous holes present in the particles, the surface area calculated from the mean radius should be less than the real surface area in contact with water, and the reaction rate should be different by the following two approaches: (1) keeping the weight of the sample at constant and changing the mean radius of the powder, (2) keeping the mean radius of the powder at constant and changing the weight of the sample. For these two approaches, reaction order obtained is the same and reaction rate is linearly dependent on the calculated surface area. It is concluded that reaction rate is mainly contributed by the reaction on the surface of the particles.

In order to avoid the interference by the reversed reaction, only the initial rate is taken into account in this experiment. Equation (3) is employed for calculation.

$$R_\text{o} = d[\text{H}_3\text{O}^+]_\text{o}/3\,dt = k[S]_\text{o}^a[\text{H}_3\text{O}^+]_\text{o}^b\,. \tag{3}$$

R_o is obtained by extrapolating the curve of the reaction rate (R) versus the reaction time (t) to $t = 0$. Keeping pH of the solution at constant, varying the surface area of Y-123, the reaction order a is obtained. Table 1 lists the relationship between the reaction temperatures, the amount of the particles, surface areas and initial rates

Table 1. At constant pH (7.00), initial reaction rate of Y-123 with water at different temperatures for powders with a mean radius of 0.0265 mm.

T/K	Weight/mg	S_o/cm^2	R_o/10^{-4} mol $\cdot$ min^{-1}
283	51.7	9.23	0.429
	100.4	17.9	0.792
	150.6	26.9	1.158
	200.9	35.9	1.583
298	54.7	9.76	1.212
	100.7	18.0	2.208
	150.6	26.9	3.193
	200.3	35.8	4.052
313	51.6	9.21	3.262
	100.5	17.9	5.941
	150.7	26.9	8.926
	200.7	35.8	11.889

for the Y-123 reaction with water. As expected, reaction rate (R_o) increases with increasing the reaction temperatures and the amount of the samples. Initial rate is found in the range of 10^{-5}–10^{-4} mol $\cdot$ min^{-1}. Plotting $\log R_o$ versus $\log [S]_o$ for the reactions of Y-123 with water at 283, 298 and 313 K at constant pH (7.00), three linear lines are obtained as shown in Fig. 1. Slopes of them are 0.95 ± 0.02, 0.93 ± 0.02 and 0.95 ± 0.02, respectively. All of them have a regression coefficient of 0.99. The average value of the slopes is 0.94 ± 0.02, very close to 1, which is used for further calculation. Slope of these lines is the reaction order of the surface area, a. In other words, reaction rate is linearly dependent on the surface area of the Y-123 powder. Reaction order a obtained for Bi-2223 is also close to 1, which is 1.01 ± 0.03.[15] First order dependence of the surface area to the reaction rate seems common for non-soluble solid.

The same method is employed for finding the reaction order of $[H_3O^+]$. Table 2 lists the data for obtaining b. R_o is obtained for each specific pH from 6.00 to 9.00. In each run, pH of the solution is kept at constant, which is controlled by the addition of the standardized $HCl_{(aq)}$ and monitored by an autotitrator. At 298 K, keeping the surface area of Y-123 powder as constant, the reaction order b is calculated from the slope of the linear line in Fig. 2. A straight line with $b = 0.318 \pm 0.002$ is obtained with a regression coefficient of 0.99. Initial rate is increased with decreasing pH of the solution. In the acidic condition, the OH^- ion produced in the reaction
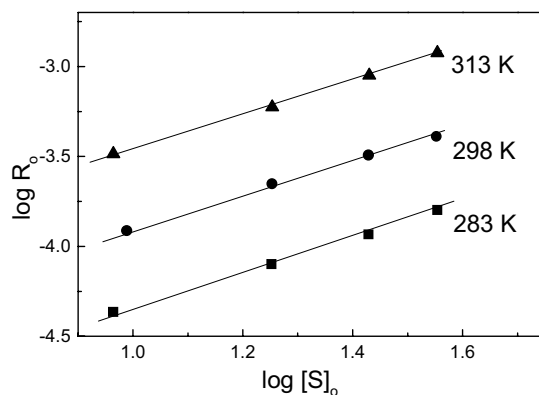

Fig. 1. $\log R_o$ versus $\log[S]_o$ for the reaction of Y-123 with water at constant pH (7.00).

Table 2.   At 298 K, initial reaction rate of Y-123 with water at different pH for powders with a mean radius of 0.0265 mm.

Weight/mg	S_o/cm^2	pH	$\log[H_3O^+]_o$	$R_o/10^{-4}$ mol $\cdot$ min^{-1}
150.6	26.9	6.00	-6.00	6.660
150.6	26.9	7.00	-7.00	3.193
150.6	26.9	8.00	-8.00	1.567
150.4	26.8	9.00	-9.00	0.733
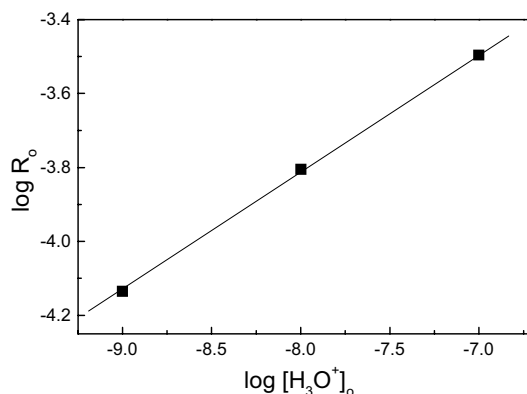
Fig. 2. $\log R_{\mathrm{o}}$ versus $\log[\mathrm{H_3O^+}]_{\mathrm{o}}$ for the reaction of Y-123 with water at 298 K.

Table 3. Rate constant for the reaction of Y-123 with water at different temperatures.

T/K	$\log k$	$k/10^{-3} \mathrm{\ mol \cdot min^{-1} \cdot cm^{-2} \cdot M^{-0.3}}$
283	-3.19	0.64 ± 0.01
298	-2.74	1.84 ± 0.02
313	-2.31	4.91 ± 0.01

is neutralized by acid and the reaction is accelerated. On the contrary, in the basic condition, OH$^-$ ion acts as an inhibitor, which suppresses the reaction. Therefore, keeping Y-123 in a basic condition is one way to reduce deterioration. The b value obtained for Bi-2223, 0.196 ± 0.004,[15] is significantly smaller than that for Y-123, suggesting that the catalytic effect of H$_3$O$^+$ ion for the reaction of Y-123 with water is greater than that for Bi-2223. Hence, the stability of Y-123 is greatly enhanced in a low [H$_3$O$^+$] condition or a high pH.

The reaction rate constant, k, is obtained from Fig. 1. The interception of the linear line to the y-axis equals to $\log k$, and k are 0.64, 1.84 and 4.91×10^{-3} mol $\cdot$ min$^{-1} \cdot$ cm$^{-2} \cdot$ M$^{-0.3}$, for the reaction at 283, 298 and 313 K, respectively, listed in Table 3. In general, the rate constant is doubled when the reaction temperature is increased by 10 K. Obviously, the reaction of Y-123 with water is typical since it increases 8 fold from 283 to 313 K. Reaction rate constants obtained for Bi-2223 at 283, 298 and 313 K are 0.399, 0.870 and 1.95×10^{-3} mol $\cdot$ min$^{-1} \cdot$ cm$^{-2} \cdot$ M$^{-0.2}$, respectively. Since k of Y-123 is larger than that of Bi-2223 at each temperature studied, the reactivity of Y-123 is clearly higher than that of Bi-2223. This is likely because Y-123 contains a stronger base, BaO, and Bi-2223 contains weaker bases, CaO and SrO. Similar conclusion is also obtained by another group.[19]

According to the Arrhenius equation,[25] $k = A \exp(-E_a/RT)$, activation energy (E_a) and pre-exponential factor (A) can be obtained from Fig. 3, which is a plot of ln k versus $1/T$. E_a calculated from the slope is 50.0 ± 0.3 kJ $\cdot$ mol^{-1} and A from
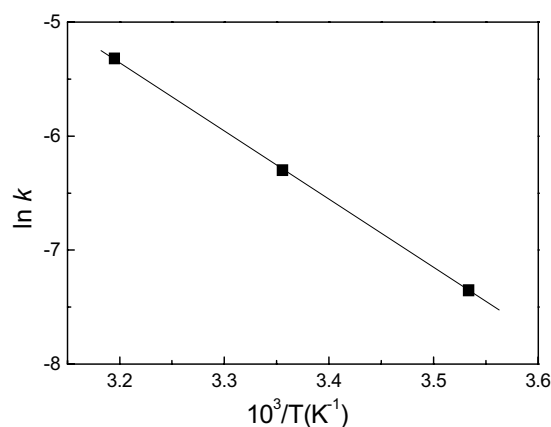
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Fig. 3. $\ln k$ versus $1/T$ for the reaction of Y-123 with water.

the intercept is 1.09×10^6 mol $\cdot$ min$^{-1} \cdot$ cm$^{-2} \cdot$ M$^{-0.3}$. A large E_a indicates that the stability in water is greatly enhanced at low temperatures. E_a and A obtained in Bi-2223 are[15] 39.1 ± 0.2 kJ $\cdot$ mol^{-1} and 6.8×10^{-3} mol $\cdot$ min$^{-1} \cdot$ cm$^{-2} \cdot$ M$^{-0.2}$. Activation energy of Y-123 reaction with water is larger than that of Bi-2223, indicating the sensitivity of Y-123 with respect to temperature is higher than that of Bi-2223. It is suggested that keeping Y-123 at a low temperatures is one way to increase its stability in water.

Acknowledgment

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