

Kinetic study of $Bi_{1.8}Pb_{0.4}Ca_2Sr_2Cu_3O_{\nu}$ superconductor in water

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The reaction of Bi_{1.8}Pb_{0.4}Ca₂Sr₂Cu₃O₂ powder in water was studied quantitatively. It was found that the $[H_3O^+]$ ion would act as a catalyst in this reaction and the initial rate equation was $R_0 = -d[A]_0/dt = k[A]_0[H_3O^+]_{0}^{8.2}$, where [A] represented the surface area of the superconducting powder. The rate constant, k, obtained at 10, 25 and 40°C was 3.98, 8.8 and 19.6×10^{-4} mol min⁻¹cm⁻²M^{0.8}, respectively. The activation energy and pre-exponential factor calculated from the Arrhenius equation were respectively 39.1 kJ mol⁻¹ and 6.4×10^3 mol min⁻¹cm⁻²M^{0.8}.

1. Introduction

Since the discovery of high- T_c superconducting materials with critical temperatures higher than the boiling point of liquid nitrogen [1], the applicability of these materials has been greatly enhanced. However, all of these superconductors contained strong bases, alkaline earth oxides, which were readily leaching out when the superconducting samples were immersed in water [2]. Moreover, the high- T_c materials were not stable even in contact with water vapor [2,3]. The reaction of $YBa_2Cu_3O_{7-x}$ with water has been qualitatively studied by several groups [2-5], for example, the pH of the aqueous solution was recorded [2] and the decomposed products were identified [2,3]. Recently, we have also qualitativelv investigated the reaction of $Bi_{1.8}Pb_{0.4}Ca_2Sr_2Cu_3O_{\nu}$ superconductor with water [6]. It was found that when the $Bi_{1.8}Pb_{0.4}Ca_2Sr_2Cu_3O_{\nu}$ powder was immersed in deionized water, a large quantity of Ca^{2+} , Sr^{2+} and OH- ions was detected in the ageous solution, indicating the decomposition of the superconductor. The chemical equation is given below:

$$Bi_{1.8}Pb_{x}Ca_{2}Cu_{3}O_{y(s)} + 4H_{2}O$$

$$\rightarrow 2 Ca_{(aq)}^{2+} + 2 Sr_{(aq)}^{2+} + 8 OH_{(aq)}^{-}$$

$$+ 0.9 Bi_{2}CuO_{4(s)} + x Cu_{6}PbO_{8(s)}$$

$$+ (3 - 0.9 - 6x) CuO_{(s)} + z O_{2(g)}. \qquad (1)$$

The x and z with respect to the amount of Pb and O_2 contents were uncertain. In general, about 30% Pb in the starting nominal composition would be lost during the preparation process due to the high volatility of PbO. The amount of oxygen evolved from the reaction should depend on the hole concentration of $Bi_{1.8}Pb_{0.4}Ca_2Sr_2Cu_3O_{\nu}$ superconductor, which is also dependent on the preparation condition, etc. As soon as the superconductor was in contact with water, the decomposition began to occur from the surface of the sample. The reaction residues remained on the surface and thereby slowed down further reaction of water with the superconductor. In this paper, we present the kinetic data of the reaction of $Bi_{1,8}Pb_{0,4}Ca_2Sr_2Cu_3O_{\nu}$ superconductor with water from the quantitative viewpoint.

2. Experimental

Pristine Bi_{1.8}Pb_{0.4}Ca₂Sr₂Cu₃O_y was prepared by a citrate precursor method described previously [7]. It had a $T_{c \text{ onset}}$, $T_{c \text{ zero}}$, ΔT_c and ρ_{295} of 115, 105, 8 K and 3.51 m Ω cm, respectively. Approximately 20–100 mg powder sample was selected by two different sieves with openings of 0.125 and 0.063 mm. The surface area and the volume of the superconducting powder were calculated by assuming the average diameter of the particles equal to the average openings

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of these two sieves. All of the solutions in this experiment contained 0.10 N NaNO₃ for ionic strength adjustment. The temperature was controlled with a circulating bath. A Radiometer Autotitrator was automatically filled with the standard solution of HCl, H_2SO_4 or HNO₃ to maintain a constant pH value. At each temperature and pH, the volume of the acid added was recorded with reaction time for calculating the reaction orders and the initial rate. The activation energy and the pre-exponential factor of the reaction were then obtained by the Arrhenius equation.

3.Results and discussion

According to the chemical equation (1) shown above, the rate equation could be written as follows:

$$R = -d[Bi_{1.8}Pb_{0.4}Ca_2Sr_2Cu_3O_y]/dt$$

= d[OH⁻]/8dt = d[Ca²⁺]/2dt = d[Sr²⁺]/2dt
= k[Bi_{1.8}Pb_{0.4}Ca_2Sr_2Cu_3O_y]^a[H_3O^+]^b. (2)

where R and k are the reaction rate and rate constant, respectively. Because Bi_{1.8}Pb_{0.4}Ca₂Sr₂Cu₃O_v was not soluble in water, its concentration could not be varied. However, its reaction rate should be proportional to its surface area represented by [A]. which could be varied either by changing the average particle size or by changing the amount of particles with a constant size. We found that both methods had the same effects on the reaction rate. In this study, the average particle size was kept constant, but the weight of Bi_{1.8}Pb_{0.4}Ca₂Sr₂Cu₃O_y powder was varied to change its surface area. Furthermore, monitoring the addition rate of [H₃O⁺] was equivalent to measuring the production rate of [OH-] of the reaction. According to eq. (2), the slope of the curve, obtained by plotting $[H_3O^+]/8$ with t, equaled the reaction rate. By extrapolating the rate to $t=0, R_0$ was obtained, where the subscript "o" represents the initial conditions. Equation (2) could also be written as

$$R_{o} = -d[A]_{o}/dt = k[A]_{o}^{a}[H_{3}O^{+}]_{o}^{b}.$$
 (3)

Therefore, by keeping the temperature and the rest variables constant, the reaction orders, a and b, could be obtained by plotting $\ln R_o$ versus $\ln [A]_o$ and $\ln R_o$

versus $\ln [H_3O^+]_{o}$, respectively. At pH=7.00, constant temperature and using HCl as the neutralization acid, a plot of $\ln R_0$ versus $\ln [A]_0$ is shown in fig. 1, where the three lines represent three different temperatures, 10, 25 and 40°C from bottom to top, respectively. The result that these lines were parallel to each other showed that temperature was the only factor affecting the reaction. Obviously, the higher the temperature, the faster was the reaction rate. The slopes calculated by the least square method were 1.03 ± 0.04 , 1.00 ± 0.01 and 0.99 ± 0.03 , respectively. The same reaction had been repeated at different pH values, such as 5.00 or 9.00, and using different neutralization agents, such as H₂SO₄ or HNO₃. The results were the same. The a values found in different conditions are listed in table 1. It is clear that the re-



Fig. 1. $\ln R_o$ vs. $\ln [A]_o$ at different temperatures.

 Table 1

 Reaction order, a, found in different conditions

Temperature/°C	pН	Acid	а
10	5.00	HC1	0.961
10	7.00	HC1	1.03
10	9.00	HC1	1.00
25	5.00	HCl	0.967
25	5.00	H ₂ SO ₄	1.03
25	5.00	HNO3	0.998
25	7.00	HCl	1.00
25	9.00	HCl	1.05
40	5.00	HCl	1.03
40	7.00	HCI	0.989
40	9.00	HCI	1.01
Average			1.01 ± 0.03

action order, a, was not changed with temperature. pH values or neutralization acids. The average order of a was 1.01 ± 0.03 . The same method was employed for finding the reaction order of $[H_3O^+]$. At constant temperature, by keeping the surface area of $Bi_{1.8}Pb_{0.4}Ca_2Sr_2Cu_3O_{\nu}$ superconducting powder constant, the order b was calculated from fig. 2 where pH was between 3.00 and 9.00 with HCl as neutralization acid at 25°C. The slope was 0.195 ± 0.002 . The standard deviation found from this straight line was only 1%. Due to the small standard deviation. it was quite reasonable to suggest that the reaction path was the same in this pH range. The same reaction had been repeated for different acids too, and the results are listed in table 2. No difference in reaction order was found in this experiment again. The average value of the reaction order, b, was 0.196 ± 0.004 . In order to simplify the rate equation. a=1.0 and b=0.2 were used instead. Thus, eq. (3) could be written as follows:

$$R_{\rm o} = -d[A]_{\rm o}/dt = k[A]_{\rm o}[H_{\rm 3}O^+]_{\rm o}^{0.2}.$$
 (4)



Fig. 2. $\ln R_o$ vs. $\ln [H_3O^+]_o$ at 25°C.

 Table 2

 Reaction order, b, found in different conditions

Temperature/°C	Acid	b
25	HCl	0.195 ± 0.002
25	H₂SO₄	0.192 ± 0.005
25	HNO ₃	0.200 ± 0.005
Average	2	0.196 ± 0.004

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The rate constants at different	temperatures and	l pl	H va	lues
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Temperature/°C	k/10 ⁻⁴	Average k		
	5.00	7.00	9.00	
10	3.99	3.98	3.97	3.98±0.01
25	8.70	8.93	8.63	8.8±0.2
40	19.5	19.7	19.6	19.6 ± 0.1

Table 4

The pre-exponential factors (A) and activation energies (E_a) at different pH

pH	$A/10^3$ mol min ⁻¹ cm ⁻² M ^{0.8}	$E_{\rm s}/{\rm kJ}{\rm mol}^{-1}$	
5.00	5.9	38.9	
7.00	6.8	39.2	
9.00	6.5	39.1	
Average	6.4 ± 0.5	39.1 ± 0.2	

It is clear from eq. (4) that the acid would accelerate the decomposition of $Bi_{1.8}Pb_{0.4}Ca_2Sr_2Cu_3O_y$ superconductor. Therefore, in order to slow down the reaction of $Bi_{1.8}Pb_{0.4}Ca_2Sr_2Cu_3O_y$ superconductor, it was better to make a large pellet with small molar surface area and to keep it in an alkaline condition.

By substituting the R_0 , $[A]_0$ and $[H_3O^+]_0$ values into eq. (4), the rate constant, k, was calculated and is listed in table 3. The k value did not depend on the pH and neutralization acids, and it was only dependent on the temperature. The pre-exponential factors and activation energies calculated according to the Arrhenius equation at different pH values are listed in table 4. The average activation energy was only 39 kJ mol⁻¹, which is quite small. This accounted for the observation that the decomposition rate was so rapid and the sample could not be prevented from reacting with water. Because of the rapid formation of OH- ions resulting from the reaction of alkaline earth cations with water, we assumed that the mole fraction of these ions in the high- T_c superconductor would probably determine its reaction rate with water.

4. Conclusion

For	the	first	time,	the	reaction	of
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 $Bi_{1.8}Pb_{0.4}Ca_2Sr_2Cu_3O_y$ superconductor with water was investigated quantitatively. The existence of the alkaline earth cations was probably the main reason for this material to be deteriorated by water. The reaction rate was proportional to the surface area of $Bi_{1.8}Pb_{0.4}Ca_2Sr_2Cu_3O_y$ superconductor and catalyzed by the hydronium ions.

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References

- [1] M.K. Wu, J.R Ashburn, C.J. Torng, P.H. Hor, R.L. Meng, L. Gao, Z.J. Huang, Y.Q. Wang and C.W. Chu, Phys. Rev. Lett. 58 (1987) 908.
- [2] N.P. Bansal and A.L. Sandkuhl, Appl. Phys. Lett. 52 (1988) 323.
- [3] M.F. Yan, R.L. Barns, H.M. O'Bryan Jr., P.K. Gallagher, R.C. Sherwood and S. Jin, Appl. Phys. Lett. 57 (1987) 532.
- [4] I. Nakada, S. Sato, Y. Oda and T. Kohara, Jpn. J. Appl. Phys. 26 (1987) L697.
- [5] J. Dominec, L. Smrcka, P. Vasek, S. Geurten, O. Smrckova, D. Sykorova and B. Hajek, Solid State Commun. 65 (1988) 373.
- [6] T.P. Wei, C.M. Wang and H.-C.I. Kao, Physica C 214 (1993) 179.
- [7] T.P. Wei, C.M. Wang and H.-C.I. Kao, J. Solid State Chem., to be published.