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Chemical durability of a superconducting oxide $YBa_2Cu_3O_x$ in aqueous solutions of varying pH values

KIYOTAKA KOMORI, HIROMITSU KOZUKA, SUMIO SAKKA
Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611, Japan

The chemical durability of a superconducting oxide $YBa_2Cu_3O_x$ in the aqueous solution was investigated as a function of pH value by measuring the amount of leaching of the cations in the solution by inductively coupled plasma (ICP) analysis. The chemical durability of $YBa_2Cu_3O_x$ was very low in highly acidic solutions of pH ca. 1, where the cations were dissolved in the same cation ratio as that of the compound. In an ion-exchanged water and NaOH solution, barium ions were leached out preferentially and almost no yttrium and copper ions were leached out. When NH_4OH was used as a basic reagent, the amounts of barium ions leached out were higher than in the NaOH solution of the same pH value and the dissolution of copper ions was observed, unlike in the NaOH solution of the same pH value. These observations were explained in terms of the chemical stability of individual oxide components.

1. Introduction

Many studies on high critical-temperature (T_c) superconducting oxides of the compositions $La_{2-x}M_xCuO_{4-y}$ (M = barium or strontium) and $YBa_2Cu_3O_x$ have been performed actively from scientific and practical aspects. The latter compound has been the subject of much recent research because of its higher T_c value, around 90 K. For materials science, the chemical durability of this compound has been found to be very important. Frase *et al.* [1] studied the chemical durability of this compound in aqueous solutions and organic solvents. Barkatt *et al.* [2] measured the rate of leaching of $YBa_2Cu_3O_x$ compound in de-ionized water and aqueous 0.05 M KI. Yan *et al.* [3] and Barns and Laudise [4] have investigated the chemical reaction between $YBa_2Cu_3O_x$ and water by X-ray diffraction technique, concluding that the superconducting compound decomposes in water to CuO, $Ba(OH)_2$ and Y_2BaCuO_5 and evolves oxygen. There is no quantitative measurement of the dissolution of the material in aqueous solutions of various pH values. In the present study, we attempted to make systematic measurements of the amount of dissolution of individual oxide component of $YBa_2Cu_3O_x$ as a function of the pH of the leaching aqueous solution, to find the nature of the chemical durability of this compound.

2. Experimental details

2.1. Preparation of samples

The superconducting oxide, $YBa_2Cu_3O_x$, was prepared in a form of polycrystalline ceramics by solid state reaction among Y_2O_3, CuO, and $BaCO_3$ powders. Given amounts of Y_2O_3 (15.1 wt %), $BaCO_3$ (52.9 wt %) and CuO (32.0 wt %) were mixed in a mortar for 1 h and 2 g of the mixture was isostatic-pressed in a rubber tube at a pressure of 660 kgw cm^{-2} to obtain a rod of ca. 20 mm × 10 mm × 3 mm. The pressed rod was heated at a rate of 5° C min^{-1} from room temperature to 750° C, kept there for 1 h for calcination, heated to 920° C at a rate of 5° C min^{-1} and kept there for 5 h. The sample was then cooled to room temperature in the furnace. A bar 7.5 mm × 6.5 mm × 2.5 mm was cut from the sintered sample and the surfaces of the bar were polished using No. 700 sand paper.

2.2. Characterization of the samples

The X-ray diffraction pattern of the sintered oxide is shown in Fig. 1. The pattern agrees with that of the superconducting oxide $YBa_2Cu_3O_x$ [5].

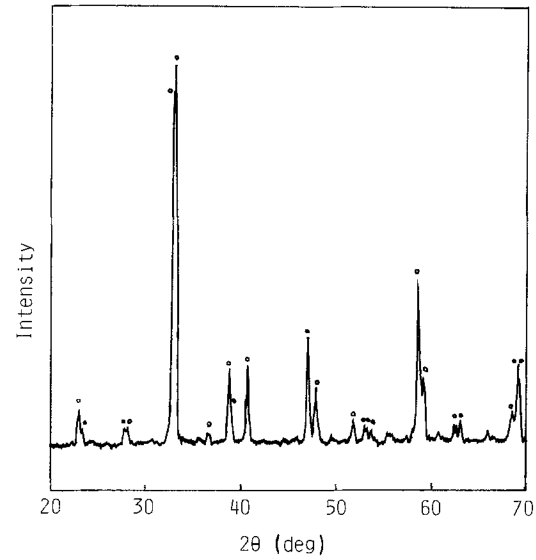

Figure 1 X-ray diffraction pattern of the $YBa_2Cu_3O_x$ sample used for the experiment. (○) denotes the peaks attributed to orthorhombic $YBa_2Cu_3O_x$ phase.

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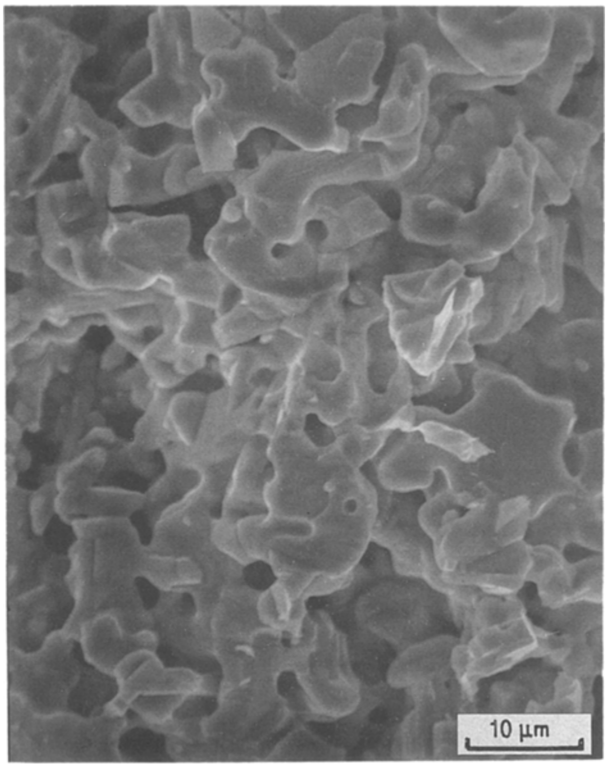

Figure 2 A SEM picture of fracture surface of the $YBa_2Cu_3O_x$ sample used for the experiment.

Figure 2 shows a micrograph by scanning electron microscopy (SEM) of fracture surface of the sintered oxide. Grains and pores at the size of about 10 μm are observed.

2.3. Chemical durability

The sample was put in a platinum basket and immersed in the aqueous solution contained in a polyethylene bottle, as shown in Fig. 3. The aqueous solution was stirred with a magnetic stirrer and kept at 20° C. The initial pH of the solution was controlled with HCl, NaOH and NH_3 solutions. 838 ml of the solution, which corresponds to 500 ml cm^{-2} of the surface area of the sample, was employed. 1 ml of the solution was extracted from the test solution at various immersion times and analysed for the amount of yttrium, barium and copper ions dissolved in the solution. The analysis was performed by ICP. Ion-exchanged water was added to the extracted solution in order to obtain enough solution for the analysis. The pH of this solution was decreased to a value < 1 by adding concentrated HCl, in order to prevent precipitation in the solution.

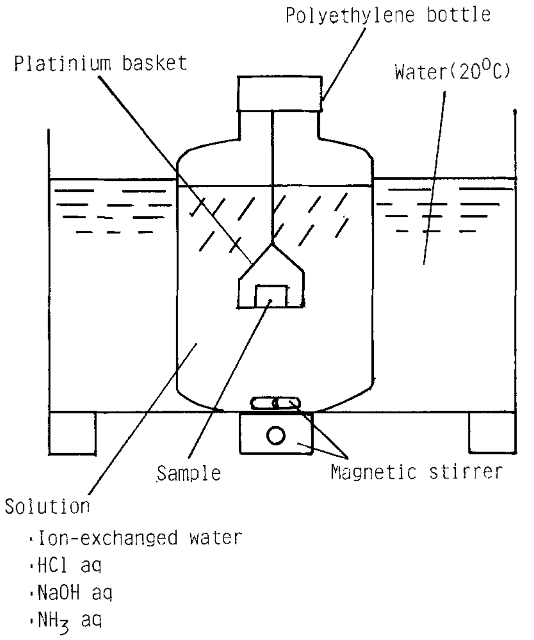

Figure 3 Arrangements for the test of chemical durability.

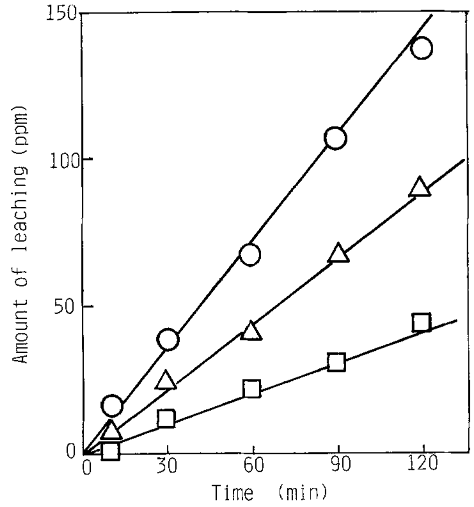

Figure 4 Amount of leaching of (○), barium, (△), copper, and (□) yttrium, ions in the solution of pH 1.0 as a function of the immersion time.

3. Results

The amount of yttrium, barium and copper ions leached in the solution of pH 1.0 at 20° C as a function of immersion time is shown in Fig. 4. It is seen that each cation is dissolved in the solution at a constant rate. The weight ratio of the dissolved cations at each time corresponds to the composition of the polycrystalline ceramics; yttrium : barium : copper = 1 : 3.09 : 2.14 in weight.

The amount of each cation leached in the solution of pH 3.0 at 20° C as a function of time is shown in Fig. 5. A different dissolution features from those in the solution of pH 1.0 can be seen; the weight ratio of the dissolved cations is not equal to that of the testing

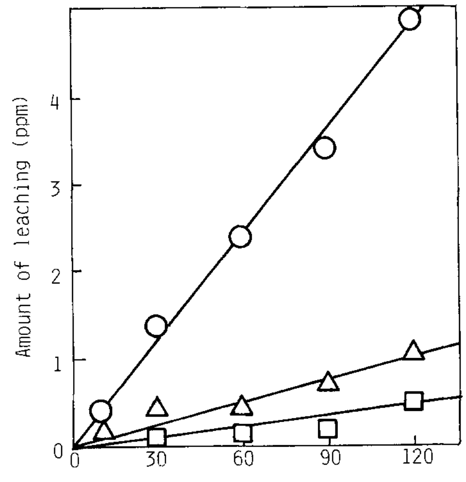

Figure 5 Amount of leaching of (○), barium, (△), copper and (□), yttrium, solution at pH 3.0 as a function of the immersion time.

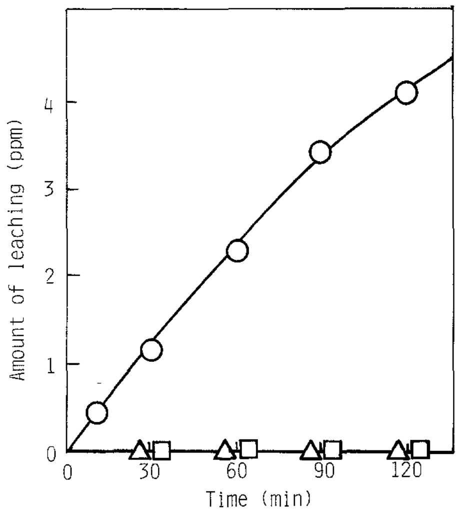

Figure 6 Amount of leaching of (○) barium, (△) copper and (□) yttrium, and ions in the solution of pH 6.6 as a function of the immersion time.

sample, i.e. barium ions are dissolved in the solution much more than yttrium and copper ions. The amounts of the leached cations are much smaller than those in the solution of pH 1.0.

The amount of each cation dissolved in the solution of pH 6.6 is shown in Fig. 6. It can be seen that barium ions are preferentially dissolved and the amounts of leaching of yttrium and copper ions are negligible (< 0.1 ppm). A similar tendency of dissolution can be found in the NaOH solution of pH 13.0, where preferential dissolution of barium ions and negligible dissolution of yttrium and copper ions are observed (Fig. 7). The amount of barium ions leached in this solution is about half of that in the solution at pH 6.6

It is interesting to see that different dissolution behaviour is observed in NaOH solution and in NH_4OH solution. Fig. 8 shows the amount of leaching of yttrium, barium and copper ions in an aqueous solution of ammonia, the pH of which is adjusted to 13.0, the same as that of the NaOH solution shown in Fig. 7. It can be seen that the amount of barium ions leached in the NH_4OH solution is about six times as large as that in the NaOH solution at the same pH and about three times as large as that in the solution at pH 3.0. The amount of dissolved copper ions was found to be about nine times as large as that in the solution at pH 3.0, whereas the amount of dissolved copper ions was negligible in the case of the NaOH solution.

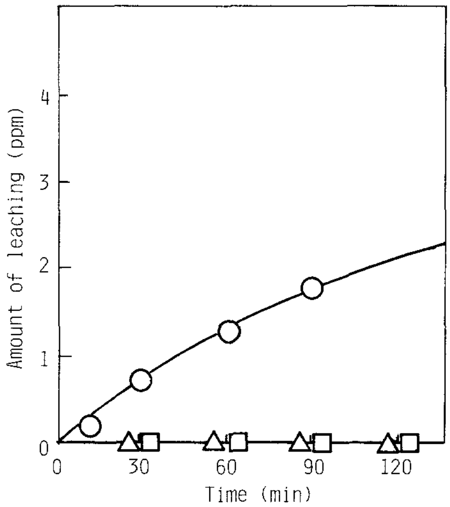

Figure 7 Amount of leaching of (○) barium, (△) copper and (□) yttrium, ions in the NaOH solution at pH 13.0 as a function of the immersion time.

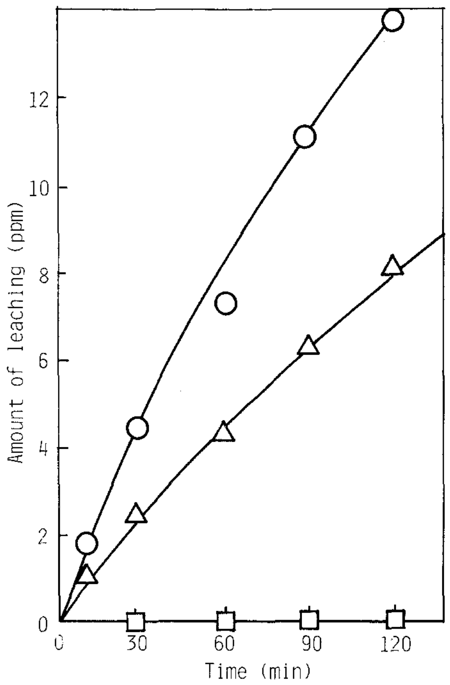

Figure 8 Amount of leaching of (○) barium, (△) copper and (□) yttrium, and ions in the NH_4OH solution at pH 13.0 as a function of the immersion time.

The amount of leaching of each cation at an immersion time of $t = 1$ h is plotted against the pH of the solution in Fig. 9, to find out the variation of the chemical durability with the pH of the solution. It can be pointed out that the leaching rate of cations increases sharply as the acidity of the solution increases below pH 3. The leaching rate of the cations gradually decreases with decreasing acidity of the solution above

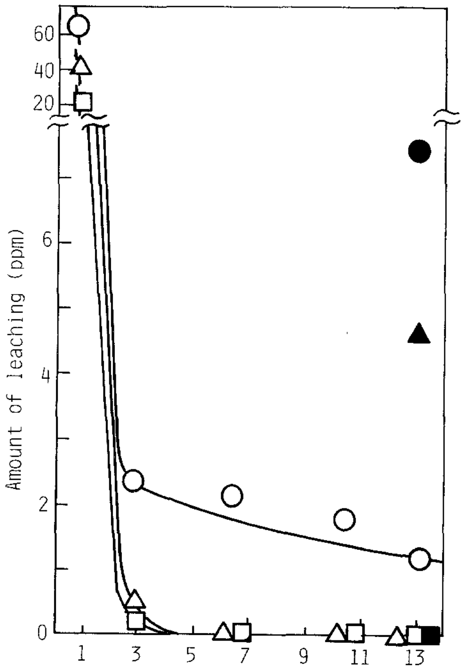

Figure 9 Dependence of the amount of leaching at the immersion time $t = 1$ h on the pH of the solution. ○ △ □: HCl for acidic solutions and NaOH for basic solutions; ● ▲ ■: NH_3 for basic solutions for barium, copper and yttrium, respectively.

TABLE I Changes of the pH of aqueous solutions by immersion

Solution	pH		
	Before immersion	After immersion	Immersion time
HCl	1.0	1.0	(2 h)
HCl	3.0	3.0	(2 h)
Ion-exchanged water	6.6	9.0	(2 h)
NaOH	10.6	10.6	(4 h)
NaOH	13.0	13.0	(2 h)
NH_4OH	13.0	13.0	(2 h)

pH 3, which can be clearly seen in the dissolution amount of barium ions. As stated before, much higher dissolution rates of barium and copper ions in the NH_4OH solution than those in the NaOH solution can also be seen in Fig. 9.

The dissolution of the cations was expected to affect the pH value of the testing solution and so the pH of the solution after immersing test was measured (Table I). It can be seen that the pH of the ion-exchanged water changes from 6.6 before immersion to 9 after 2 h immersion. No change in pH value is seen in the other acidic or basic solutions.

4. Discussion

Paul and Youssefi [6, 7] reported that in principle the thermodynamic stability of a glass towards aqueous solutions may be a function of the activity of the oxide components in the glass and the stability of individual oxides towards hydration, ionization and complexation in aqueous solutions. When the activity of ionic species are higher than those of oxide and hydrated oxide, the oxide is dissolved easily. In the reverse case, dissolution of the oxide is difficult. This idea is adapted to the present study.

Possible chemical reactions of the oxide component in aqueous solutions are listed in Table II. The standard free energies of these reactions (ΔG^0) were calculated using the standard chemical potentials [8, 9] for each species. The equilibrium constant K was calculated using the relation $\Delta G^0 = -RT \ln K$, where R is the gas constant and T is the absolute temperature and the relationship between the activity of chemical species was drawn as shown in the last column of the table.

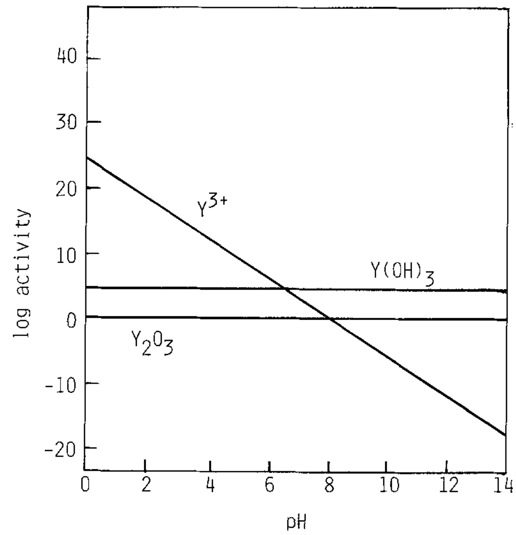

Figure 10 Stability of Y_2O_3 in the aqueous solution at different pH (25° C).

As an example, the reaction between water and BaO may be presented as:

$$BaO + H_2O = Ba(OH)_2$$

$$K = \frac{a_{Ba(OH)_2}}{a_{BaO}a_{H_2O}}$$

ΔG^0 of the reaction is $-90.9\,\text{kJ mol}^{-1}$, and therefore:

$$\log K = 15.9.$$

Here the activities of the oxides and water were set at 1 as standards. Therefore:

$$\log[Ba(OH)_2] = 15.9.$$

The dissociation of barium hydroxide can be written as:

$$Ba(OH)_2 = Ba^{2+} + 2OH^-$$

$$K = \frac{a_{Ba^{2+}}a^2_{OH^-}}{a_{Ba(OH)_2}}$$

ΔG^0 of the reaction is $-18.9\,\text{kJ mol}^{-1}$ and $\log K = 3.3$.

$$\log[Ba^{2+}] = 19.2 + 2pOH = 47.2 - 2pH.$$

Using these equations, the diagram of stability of BaO in an aqueous solutions can be drawn as shown in Fig. 11. Figures 10, 12 and 13 are made also by using the calculations in the same way. For the data in

TABLE II Thermochemical data for reactions of some major component oxide of $YBa_2Cu_3O_x$ compound with aqueous solution at 25° C

Reaction	ΔG^0 (kJ mol^{-1})	log K	Relationship
$1/2Y_2O_3 + 2/3H_2O = Y(OH)_3$	−27.7	4.8	$\log[Y(OH)_3] = 4.8$
$Y(OH)_3 = Y^{3+} + 3OH^-$	126.3	−22.1	$\log[Y^{3+}] = 24.7 - 3pH$
$BaO + H_2O = Ba(OH)_2$	−90.9	15.9	$\log[Ba(OH)_2] = 15.9$
$Ba(OH)_2 = Ba^{2+} + 2OH^-$	−18.9	3.3	$\log[Ba^{2+}] = 47.2 - 2pH$
$CuO + H_2O = Cu(OH)_2$	116.1	−20.3	$\log[Cu(OH)_2] = -20.3$
$Cu(OH)_2 = Cu^{2+} + 2OH^-$	1.7	−0.3	$\log[Cu^{2+}] = 7.4 - 2pH$
$CuO + NH_4^+ = Cu(NH_3)^{2+} + OH^-$	67.5	−11.8	$\log[Cu(NH_3)^{2+}] = -11.8$*
$CuO + 2NH_4^+ = Cu(NH_3)_2^{2+} + H_2O$	21.0	−3.6	$\log[Cu(NH_3)_2^{2+}] = -31.6 + 2pH$*
$CuO + 3NH_4^+ = Cu(NH_3)_3^{2+} + H_2O + H^+$	57.6	−10.1	$\log[Cu(NH_3)_3^{2+}] = -52.1 + 4pH$*
$CuO + 4NH_4^+ = Cu(NH_3)_4^{2+} + H_2O + 2H^+$	98.9	−17.2	$\log[Cu(NH_3)_4^{2+}] = -73.3 + 6pH$*
$CuO + 5NH_4^+ = Cu(NH_3)_5^{2+} + H_2O + 3H^+$	15.5	−27.0	$\log[Cu(NH_3)_5^{2+}] = -97.2 + 8pH$*

*. . . calculated as $[OH^-] = [NH^{4+}]$

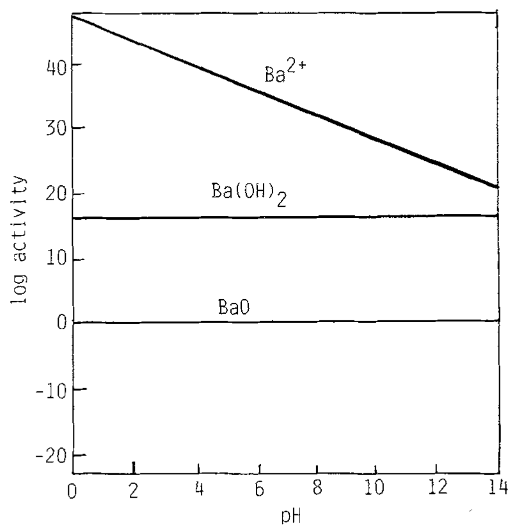

Figure 11 Stability of BaO in the aqueous solution at different pH (25° C).

Fig. 13, equations were derived with the assumption that the activity of NH^{4+} was equal to that of OH$^-$.

Preferential dissolution of barium ions was observed in the neutral and basic solutions. It can be seen in Figs. 10 and 12 that stabilities of soluble species, Y^{3+} and Cu^{2+}, are higher than those of Y(OH)$_3$ and CuO in the pH range of pH < 6.6 and pH < 3.7, respectively. On the other hand, Fig. 11 shows that Ba^{2+} is stable in the whole pH range. Thus, preferential dissolution of barium ions observed in neutral and basic solutions can be explained by the differences in the stability of ions relative to insoluble species.

Gradual decrease in the amount of leached barium ions with increasing pH in the pH region of pH > 3, shown in Fig. 9, can be attributed to a decrease in the stability of Ba^{2+} with increasing pH (Fig. 11). However, an extreme decrease in dissolution rate of barium ions with increasing pH observed at pH 3 cannot be explained from the thermodynamic stability of Ba^{2+} ions alone. To explain this, the kinetic factor should be considered. Insoluble species CuO and Y(OH)$_3$ become stable in the pH range of pH > 3.7 and pH > 6.6, respectively, as expected from the diagram of activity (Figs. 10 and 12) this is reflected in the decrease of dissolution rate of copper and yttrium ions at pH 3. These insoluble species would prevent the leaching of barium ions.

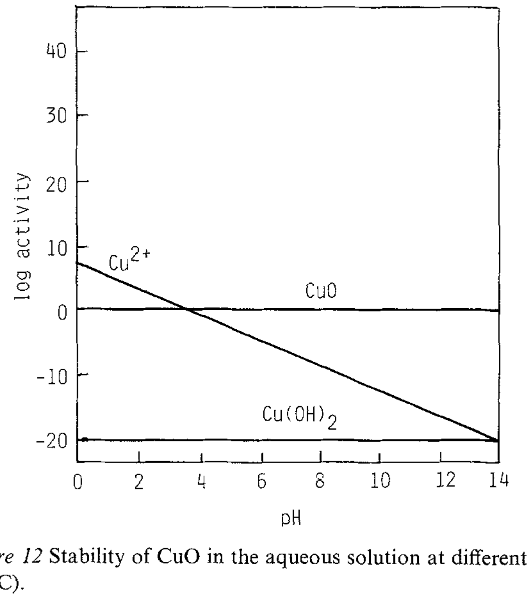

Figure 12 Stability of CuO in the aqueous solution at different pH (25° C).

Paul [6] states that the dissolution of divalent ions like Ba^{2+} by diffusion is quite difficult. This indicates that the extreme decrease in the dissolution rate of barium ions accompanying that of copper and yttrium ions can be attributed to the difficulty in diffusion of barium ions in the solid. It can be considered that as for the dissolution of barium ion, the kinetic stability, i.e. difficulty of leaching by diffusion, is more predominant than thermodynamic stability. Since copper and yttrium ions are stable in the lowest pH range (pH 1), it can be considered that the rate of dissolution of barium ions corresponds to the rate of formation of a new surface by the dissolution of copper and yttrium ions following the leaching of barium ions. This would make the possible dissolution of cations in the same cation ratio as that of the tested compound.

In the NH$_4$OH solution of pH 13, the rate of dissolution of copper ions is much larger than in the NaOH solution of the same pH value. This can be understood from the diagram shown in Fig. 13; complex species of Cu(NH$_3$)$_4^{2+}$ and Cu(NH$_3$)$_5^{2+}$ become stable in the pH range of pH > 12. Formation of ammonium complex ions gives rise to high dissolution rate of copper ions in the NH$_4$OH solution, which is not possible in the NaOH solution. Also the dissolution of barium ions, which is thought to be possible on the basis of thermodynamic stability of Ba^{2+}, is accelerated by the dissolution of the major component, copper. On the other hand, yttrium ions, which are not stable in such a high pH range, cannot be dissolved even when ammonia is used as a base.

5. Conclusion

Chemical durability of the superconducting oxide YBa$_2$Cu$_3$O$_x$ under aqueous solutions of various pH values was studied by measuring the leaching amount of cation components in the solutions.

1. The chemical durability of YBa$_2$Cu$_3$O$_x$ was found to be quite low in highly acidic solution of pH ca. 1, where dissolution occurs in the same cation ratio as that of the compound.
2. The rate of dissolution of the material decreased

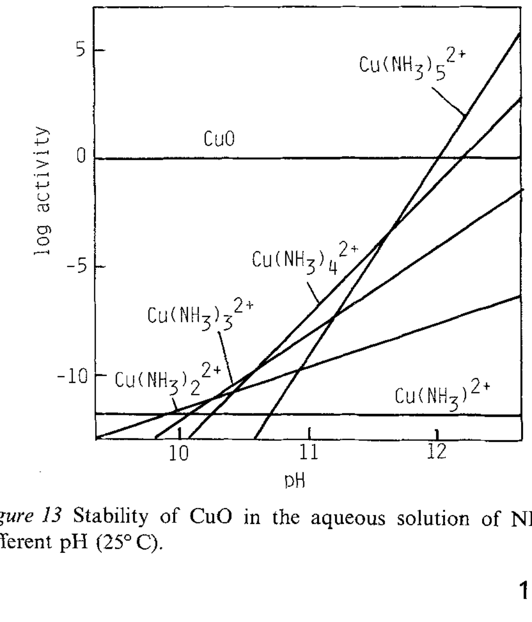

Figure 13 Stability of CuO in the aqueous solution of NH$_3$ at different pH (25° C).

sharply with increasing pH at pH ca. 3, which could be attributed to the instability of Cu^{2+} and Y^{3+} compared with those of CuO and $Y(OH)_3$ above pH 3.7 to 6.6.

3. When NaOH was used as a basic reagent in the solution, preferential dissolution of barium ions was observed in neutral and basic solutions. This could be explained by thermodynamic stability of Ba^{2+}; CuO and $Y(OH)_3$ are thermodynamically more stable than Cu^{2+} and Y^{3+}.

4. When NH_4OH was used as a basic reagent in the solution, the dissolution rate was larger than in the case of NaOH solution. Formation of $Cu(NH_3)_4^{2+}$ or $Cu(NH_3)_5^{2+}$ is thought to lead to higher rate of dissolution of the material.

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