JOURNAL OF MATERIALS SCIENCE 31 (1996) 2975–2979

Superconducting properties of the lithium-substituted $YBa_2Cu_4O_8$ prepared by the sol-gel method

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The effects of the lithium substitution for copper on the properties of the superconducting $YBa_2Cu_4O_8$ were studied. Single-phase $YBa_2Cu_{4-x}Li_xO_8$ was successfully prepared by the sol-gel method under ambient pressure over a composition range of $0 \leqslant x \leqslant 0.08$, while impurity phases appeared at $x=0.10$ and 0.20. The lattice constants of $YBa_2Cu_{4-x}Li_xO_8$ were almost invariant with increasing lithium content x. The superconducting transition temperature decreased monotonically with increasing x in the range, $0 \leqslant x \leqslant 0.08$. The suppression of superconductivity was discussed in terms of the impurity effect in the CuO_2 planes.

1. Introduction

In the investigation of the superconductivity mechanism in copper oxide based high T_c superconductors, one of the significant approaches is to study the effects of the replacement of copper by other elements, because it directly affects the electronic and magnetic structure of the CuO_2 planes, which are believed to be responsible for the electrical conduction of these compounds. According to previous studies [1, 2], the substitution at copper sites drastically lowers the superconducting transition temperature, T_c, regardless of the kind of substituting elements, even if the amount of substituents is very small. The destruction of superconductivity is attributed to the appearance of magnetic moment caused by the substitution [3], that is, the substituents at copper sites are thought to act as magnetic impurities.

Among the substituents at copper sites, however, lithium shows some interesting effects. Kawai *et al.* [4] reported that T_c of the Bi-2212 superconductor increases on the addition of lithium, which is considered to be substituted for copper. This result attracted much attention because it is the only case where substitution at copper sites can raise T_c. The reason for the increase in T_c caused by the addition of lithium, however, has not been clearly explained because of the difficulty in obtaining single-phase superconductors in the Bi–Sr–Ca–Cu–O system; i.e. the bismuth system has three superconducting phases, the Bi-2223, Bi-2212 and Bi-2201 with T_c of 110, 80 and 8 K, respectively, and none of them can be easily obtained as a pure single phase. In addition, there are two cations (bismuth and copper) with variable valences. Consequently, the increase in T_c by lithium addition has been attributed to the change of cation ratio, the change of the amount of Bi-2223 phase or the change of carrier concentration.

In $YBa_2Cu_3O_{7-\delta}$ (Y-123), which can be easily produced as a single phase, Feduzi *et al.* [5] reported that the lithium substitution for copper causes a decrease in T_c, where they attributed the decrease in T_c to the decrease in the hole concentration caused by the larger oxygen loss than expected from the charge compensation. Noting that $YBa_2Cu_4O_8$ (Y-124) has a much more stable oxygen content up to 850 °C than Y-123 [6], it is interesting to ascertain in Y-124 whether substitution of lithium for copper results in the formation of oxygen vacancies and/or a change in hole concentration and how it affects the superconductivity. It should also be noted that in Y-124 the substitution of Ca^{2+} for Y^{3+} increases the hole concentration and hence T_c [7], while the substitution of K^+ or Na^+ for Ba^{2+} does not change the hole concentration [8]. We do not know, however, what will happen when copper is replaced by lithium in Y-124.

In the present work, we examined the effects of the lithium substitution for copper on the superconductivity of $YBa_2Cu_4O_8$ in order to clarify the role of lithium as a dopant to copper oxide superconductors. $YBa_2Cu_{4-x}Li_xO_8$ was prepared by the sol-gel method [9] under 1 atm oxygen, and the lattice constants, the oxygen content, and the temperature dependence of the electrical resistance and the magnetic susceptibility were measured.

2. Experimental procedure

Samples were prepared by the sol-gel method using metal acetates as starting materials. $Y(CH_3COO)_3 \cdot 4H_2O$ (Mitsuwa Pure Chemicals, Osaka, Japan), $Ba(CH_3COO)_2$ (Wako Pure Chemicals, Osaka, Japan), $Cu(CH_3COO)_2$ (Wako Pure Chemicals) and $CH_3COOLi \cdot H_2O$ (Wako Pure Chemicals) were dissolved in distilled water to make an aqueous solution with a cation molar ratio of Y:Ba:Cu:Li = 1:2:(4 − x):x (x = 0, 0.03, 0.05, 0.08, 0.10 and 0.20). After stirring for 1 h, an aqueous solution of tartaric acid ($C_4H_6O_6$) was added to the acetates solution. The molar ratio $C_4H_6O_6$/Cu was fixed at 0.43. The resultant solution was stirred for another 2 h and concentrated in an oven at 80 °C. After 2 days, a dried gel with blue colour was obtained. The gel was pulverized, heated to 780 °C at a rate of 2.5 °C min^{-1} in flowing oxygen of 1 atm, kept at 780 °C for 2 h and cooled in the furnace. The resultant black powder was pressed into pellets with 13 mm diameter and about 1 mm thick under a pressure of 60 MPa and heated at 780 °C for 30–50 h with occasional grinding and pelletizing. For comparison, the lithium-free and copper-deficient sample of the nominal composition $YBa_2Cu_{3.92}O_8$ was also prepared by the same process as described above.

The crystalline phases evolved in the samples after the heat treatment were identified by the powder X-ray diffraction (XRD) method with a Rigaku Denki Company model RAD-IIA diffractometer using CuK_α radiation. The lattice constants of the Y-124 phases were determined by the internal standard method using silicon. The oxygen content of some samples was determined by the iodometric titration technique, which was described elsewhere [8]. The d.c. electrical resistance of the samples was measured by a four-probe method at temperatures from 300–50 K with a Chino Instrument Company superconductivity test system. The a.c. magnetic susceptibility of the samples was measured by a Hartshorn bridge method.

3. Results

3.1. Formation of the Y-124 phases

Fig. 1 shows the X-ray diffraction (XRD) patterns of the $YBa_2Cu_{4-x}Li_xO_8$ samples with x varying from 0 to 0.20. The lithium-free Y-124 phase was obtained as a single phase by heating the gel at 780 °C for 30 h in flowing oxygen. The lithium-substituted Y-124 samples with x = 0.03, 0.05 and 0.08 were also obtained as a single phase by the same heat treatment as that for the lithium-free Y-124 sample. On the other hand, impurity phases remained in the samples and a single phase of the Y-124 was not obtained for x = 0.10 and 0.20, even when the heating time was prolonged for up to 50 h. Oxygen contents of both the pure Y-124 and the lithium-substituted Y-124 of x = 0.08 were determined to be 8.0 by iodometric titration.

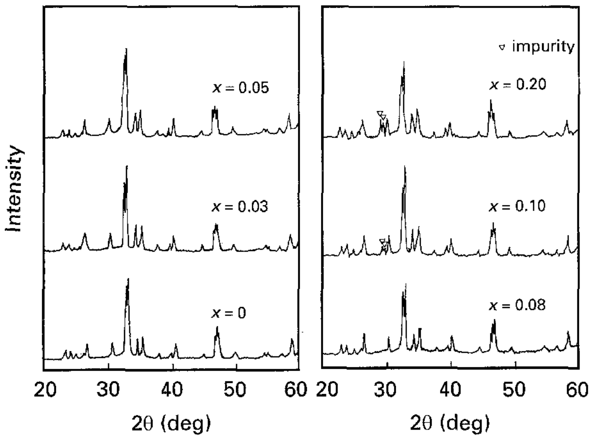

Figure 1 The XRD patterns of the $YBa_2Cu_{4-x}Li_xO_8$ ($0 \leqslant x \leqslant 0.20$) samples obtained by heating the gel at 780 °C for 30 h in flowing oxygen.

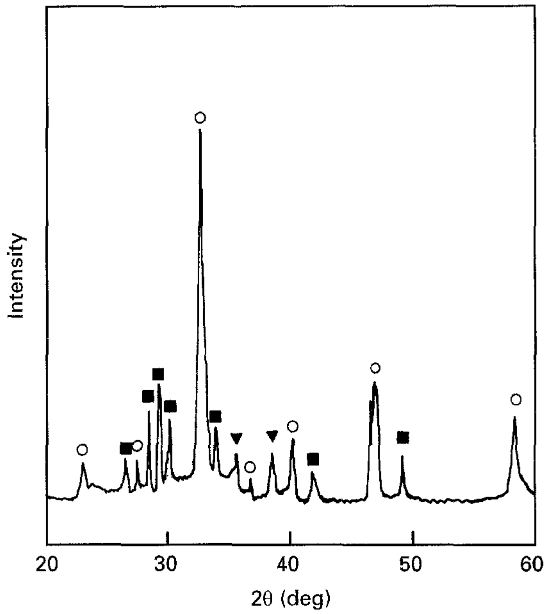

Figure 2 The XRD pattern of the sample of the nominal composition $YBa_2Cu_{3.92}O_8$ obtained by heating the gel at 780 °C for 30 h in flowing oxygen. (○) $YBa_2Cu_3O_7$, (■) $BaCuO_2$, (▼) CuO.

Fig. 2 shows the XRD pattern of the lithium-free, copper-deficient $YBa_2Cu_{3.92}O_8$ sample heated at 780 °C for 30 h in O_2. It is seen that the Y-124 phase was not formed and, instead, Y-123, $BaCuO_2$ and CuO were formed.

3.2. Lattice constants

The lattice constants a, b and c of the lithium-substituted Y-124 phases are summarized in Table I and shown in Fig. 3. The values for the lithium-free Y-124 are a = 0.3846, b = 0.3869 and c = 2.721 nm, which are in good agreement with those reported previously [10, 11]. It is seen from Fig. 3 that all the lattice constants a, b and c hardly change with increasing lithium content, x.

3.3. Electrical resistance and magnetic susceptibility

The temperature dependences of the electrical resistance of $YBa_2Cu_{4-x}Li_xO_8$ with x = 0, 0.03, 0.05 and 0.08 are shown in Fig. 4. All the samples show metallic conductivity with decreasing temperature and superconducting transition at 75–83 K. Fig. 5 shows T_c (onset) and T_c (end) plotted against lithium content, x. T_c (onset) decreases monotonically with increasing x up to 0.05, remains constant from x = 0.05 to 0.10 and decreases again at x = 0.20. T_c (end) decreases similarly with increasing x up to 0.05 and then keeps a constant value of 66 K from x = 0.05 to 0.20. Note that the samples of x = 0.10 and 0.20 are not the single phase of Y-124.

TABLE I Lattice constants and superconducting transition temperatures of $YBa_2Cu_{4-x}Li_xO_8$

Lithium content, x	Lattice constants (nm)			T_c (onset) (K)	T_c (end) (K)	T_c (χ) (K)
	a	b	c			
0	0.3846	0.3869	2.721	83	77	75
0.03	0.3844	0.3867	2.722	78	72	69
0.05	0.3848	0.3868	2.721	75	66	64
0.08	0.3846	0.3868	2.723	75	66	64
0.10[a]	0.3844	0.3868	2.724	75	66	63
0.20[a]	0.3847	0.3868	2.723	70	66	59

[a] Including impurity phases other than Y-124 phase.

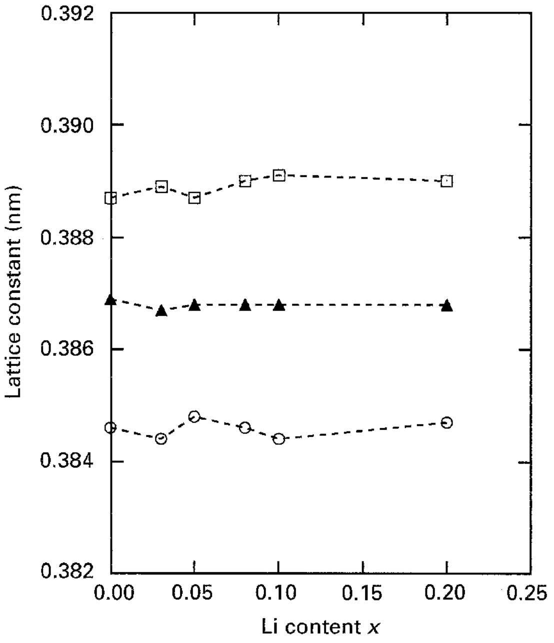

Figure 3 The lattice constants (○) a, (▲) b and (□) $c/7$ of the $YBa_2Cu_{4-x}Li_xO_8$ ($0 \leqslant x \leqslant 0.20$) samples plotted against the lithium content.

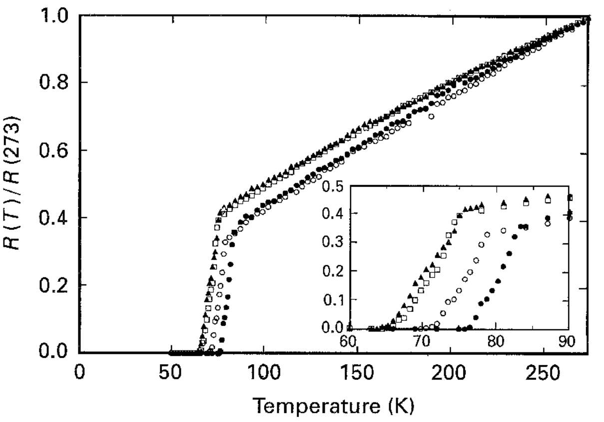

Figure 4 The temperature dependences of the electrical resistance of the $YBa_2Cu_{4-x}Li_xO_8$ samples, x: (●) 0, (○) 0.03, (▲) 0.05, (□) 0.08.

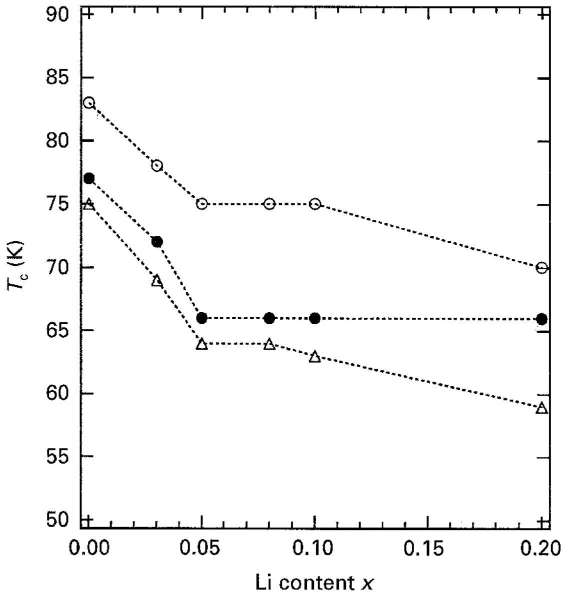

Figure 5 The superconducting transition temperatures, (○) T_c (onset), (●) T_c (end) and (△) T_c (χ) of the $YBa_2Cu_{4-x}Li_xO_8$ samples plotted against the lithium content, x.

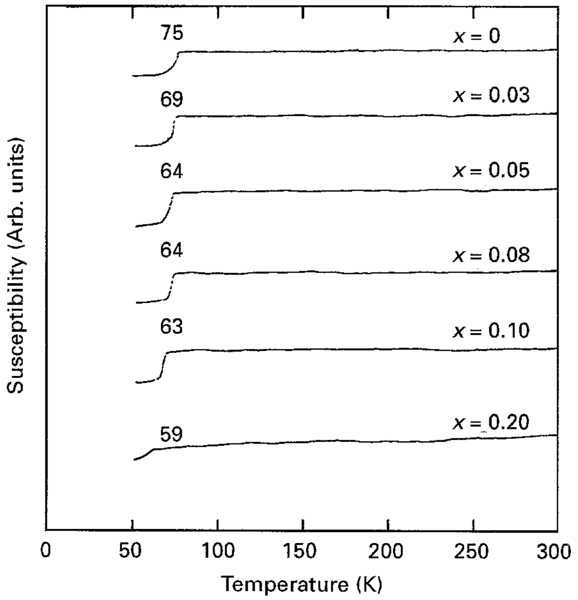

Figure 6 The temperature dependences of the a.c. magnetic susceptibility of the $YBa_2Cu_{4-x}Li_xO_8$ samples.

Fig. 6 shows the temperature dependences of the a.c. magnetic susceptibility of $YBa_2Cu_{4-x}Li_xO_8$. It is seen that diamagnetism appears in all the samples at temperatures 2–6 K lower than T_c (end) observed in electrical resistance. Superconducting transition temperature, T_c (χ), which was determined from the susceptibility curve, is plotted against lithium content, x, in Fig. 5. $T_c(\chi)$ decreases in a similar manner to T_c (onset) as the lithium content, x, increases from $x = 0$ to 0.20.

4. Discussion

4.1. Effects of lithium substitution on the formation and structure of Y-124

As seen from Fig. 2, the copper-deficient composition of $YBa_2Cu_{3.92}O_y$ does not form the Y-124 phase. As we reported previously [12], there are two key reaction routes for the formation of Y-124 phase from the gel, which proceed simultaneously, as described in the following formulas

$$YBa_2Cu_3O_y + CuO + [(7 - y)/2]O_2 \rightarrow YBa_2Cu_4O_8 \quad (1)$$

$$(1/2)Y_2Cu_2O_5 + Ba_2Cu_3O_{5.9} \rightarrow YBa_2Cu_4O_8 + (1/5)O_2 \quad (2)$$

It should be noted, however, that in the $YBa_2Cu_{3.92}O_y$ gel a large amount of $BaCuO_2$ is precipitated in addition to $YBa_2Cu_3O_y$ and CuO when the gel is heated at 780 °C for 30 h, and there is no $Ba_2Cu_3O_{5.9}$ precipitated, which is an important intermediate for the Y-124 formation. These indicate that Reaction 2 cannot take place because of the absence of $Ba_2Cu_3O_{5.9}$ and the rate of Reaction 1 is much lowered by the large amount of $BaCuO_2$ grains preventing the $YBa_2Cu_3O_y$ and CuO grains from coming into contact with each other. On the contrary, the composition of $YBa_2Cu_{3.92}Li_{0.08}O_8$, where the copper-deficient sites are considered to be occupied by lithium in $YBa_2Cu_{3.92}O_y$ composition, could form the single-phase Y-124 as shown in Fig. 1. It can be said, therefore, that lithium can work as the substituent for copper, which results in the formation of the Y-124 phase in the $YBa_2Cu_{3.92}Li_{0.08}O_8$ composition.

According to the report by Feduzi *et al.* [5], 10% of the copper can be replaced by lithium in the $YBa_2Cu_3O_y$ samples through the solid-state reaction. On the other hand, the present $YBa_2Cu_{4-x}Li_xO_8$ samples showed the solubility limit of lithium around $x = 0.08$, which corresponds to 2% of copper. Therefore, it is likely that lithium can more easily substitute for copper in the Y-123 phase than in the Y-124. The difference in the solubility of lithium between the Y-123 and the Y-124 phases may arise from the difference in their formation processes as well as their structural difference; Y-124 has more complicated formation process than Y-123, as mentioned above.

$YBa_2Cu_4O_8$ has two different copper sites that can be replaced by lithium, namely Cu(1) in the double CuO chains and Cu(2) in the CuO_2 planes. According to Felner and Brosh [13], iron ions occupy preferentially the Cu(1) sites while zinc ions prefer the Cu(2) sites, and it is likely that the valence of the substituent ions determines the copper sites to be occupied. That is, ions with valences higher than +2 tend to occupy the Cu(1) site, while those with +2 or +1 tend to occupy the Cu(2) site. Therefore, it is probable that Li^+ ions occupy the Cu(2) site in the present samples. It should be mentioned that in Y-123, Li^+ ions substitute for the Cu(2) in the CuO_2 planes as reported by Feduzi *et al.* [5].

As seen in Fig. 3, the lattice constants remain almost invariant with changing x in $YBa_2Cu_{4-x}Li_xO_8$, which may result from the similar ionic radius between Cu^{2+} (0.73 nm) and Li^+ (0.76 nm) [14]. Feduzi *et al.* [5] reported that the lattice constant c slightly decreases with increasing lithium content in the Y-123. In the present Y-124, however, no significant change was observed in the lattice constant c by the lithium substitution. This is primarily due to the lower solubility of lithium, which is one-fifth of that in the Y-123.

4.2. Changes in the superconducting properties by the lithium substitution

The formal charge of copper in the $YBa_2Cu_{4-x}Li_xO_8$ sample with $x = 0.08$ is determined to be +2.27 by iodometric titration, which is slightly higher than that in $YBa_2Cu_4O_8$, +2.25. Such an increase in the formal copper charge which was also observed in the calcium-substituted $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$, +2.275, clearly indicates that additional holes were introduced in this compound. However, in contrast to the fact that calcium substitution can raise T_c of the Y-124 from 80 K to 90 K [7], the present lithium-substituted samples exhibited the decrease in T_c with increasing lithium content x as shown in Fig. 5. Therefore, it is considered that the substitution at the copper-site in Y-124 is crucial to the superconductivity even in the case of lithium substitution; that is, the substituents for copper always diminish T_c or destroy superconductivity of the Y-124 superconductor.

Xiao *et al.* [3] reported that the substitution at copper sites in $La_{2-x}Sr_xCuO_4$ reduced T_c regardless of the magnetic or non-magnetic substituents and interpreted this as a result of the emerging magnetism in the CuO_2 planes that arises from $S = 1/2$ spin of Cu^{2+}, which bring about the magnetic pair-breaking effect. Felner and Brosh [13] reported that in the Y-124, both magnetic iron ions at the Cu(1) site and non-magnetic zinc ions at the Cu(2) site largely suppress superconductivity. Because Li^+ ions are not magnetic, the decrease in T_c in the present samples is probably attributed to the substitution of lithium at the Cu(2) site, which probably generates the magnetic moment in the CuO_2 planes. Unless lithium is substituted for copper at the Cu(2) site, T_c might increase because of the introduced holes.

The decreasing rate of T_c, dT_c/dx, in the present $YBa_2Cu_{4-x}Li_xO_8$ is about -1.4×10^2 K, which is smaller than that in $YBa_2Cu_{4-z}M_zO_8$ (M = Fe, Zn) [12], $dT_c/dz \approx -6.9 \times 10^2$ K. This may result from the effects of valence of the substituents occupying the copper sites. Malik *et al.* [15] reported that the substitution of silver for copper in $La_{1.8}Sr_{0.2}Cu_{1-x}Ag_xO_{4-\delta}$ depressed T_c by 50% at $x = 0.15$, which is much less than the effect of the other substituents such as iron, cobalt, nickel, zinc, etc. [3]. Because silver is ordinarily a monovalent ion as is lithium in the present case, it is very likely that the substitution of the monovalent ions for copper is less effective in suppressing superconductivity than ions with a valence of more than +1. This is thought to result from the effect of the holes introduced by the substitution, that is, the holes may suppress the appearance of the Cu^{2+} spin.

5. Conclusion

The single-phase superconducting $YBa_2Cu_{4-x}Li_xO_8$ was successfully prepared by the sol-gel method, and the effects of the lithium substitution on the formation, structure and superconducting properties were examined. A single phase of the Y-124 was obtained in the range $0 \leqslant x \leqslant 0.08$, while impurity phases appeared over $x = 0.10$. The lattice constants were almost constant with increasing x, probably due to the similar ionic radius between Cu^{2+} and Li^{+}. The superconducting transition temperature decreased with increasing lithium content. The suppression of superconductivity by the lithium substitution was attributed to the impurity effect in the CuO_2 planes, which gives rise to the magnetic moment.

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*Received 20 February
and accepted 1 December 1995*