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Kyoto University
Effects of Substitution of Sr, K or Na for Ba on the Structure and Properties of Gel-Derived YBa$_2$Cu$_4$O$_8$ Superconducting Oxide

Shinobu Fujihara*, Toshiyuki Nakata*, Hiromitsu Kozuka* and Sumio Sakka*

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Single-phase YBa$_{2-x}$R$_x$Cu$_4$O$_8$ (R = Sr, K, Na) superconductors were successfully prepared by heating gels of the target compositions in 1 atm oxygen, and the effects of substitution of Sr, K or Na for Ba on the $T_c$, lattice constants, oxygen content and microstructure were examined. Sr could be substituted for 20% of Ba in YBa$_2$Cu$_4$O$_8$ and the lattice constants $a$, $b$ and $c$ decreased monotonically with increasing Sr concentration. $T_c$ (onset) and $T_c$ (end) of YBa$_{2-x}$Sr$_x$Cu$_4$O$_8$ were 3 K higher and 2 K higher than those of YBa$_2$Cu$_4$O$_8$, respectively. K could be substituted for 10% of Ba and the lattice constant $a$ slightly decreased with increasing K concentration, whereas $b$ and $c$ remained constant. $T_c$ of YBa$_{2-x}$K$_x$Cu$_4$O$_8$ was slightly lower than that of YBa$_2$Cu$_4$O$_8$. Na could be substituted for 5% of Ba and the lattice constant $a$ decreased with increasing Na concentration, whereas $b$ and $c$ remained constant. $T_c$ (end) of YBa$_{2-x}$Na$_x$Cu$_4$O$_8$ was 4 K higher than that of YBa$_2$Cu$_4$O$_8$. Grain growth was observed in the K- and Na-substituted samples. Changes of $T_c$ by the substitution were discussed in terms of the contraction of the lattice, the formation of oxygen vacancies, the concentration of holes and the role of grain boundaries.

**KEY WORDS:** YBa$_2$Cu$_4$O$_8$/ Sol-gel method/ Superconductor/ Substitution/ Lattice constants/ Oxygen content

1. INTRODUCTION

In the Y-Ba-Cu-O oxide system, there are two important superconducting phases, YBa$_2$Cu$_3$O$_{7-δ}$ (123) and YBa$_2$Cu$_4$O$_8$ (124), which differ in the number of CuO chains in the structure.$^{1-3}$ The 123 phase has single CuO chains and its oxygen content depends on the conditions of preparation such as the heat-treatment temperature, the partial oxygen pressure in the heat-treatment atmosphere and the cooling rate. Superconducting transition temperature $T_c$ of the 123 phase decreases from 90 K as the oxygen content decreases. On the other hand, the 124 phase has double CuO chains and its oxygen content is almost constant up to 850°C. $T_c$ of the 124 phase is about 80 K,$^{4,5}$ which is not affected by the preparation conditions.

It is known that the application of high pressure at measurement affects the $T_c$ of the 124 phase much more markedly than that of the 123 phase. Bucher et al.$^5$ first reported that $T_c$ of the 124 phase increases with pressure, $p$, at a rate of $dT_c/dp = 5.5$ K/GPa. Yamada et al.$^6$ also reported the same value of $dT_c/dp$ in the 124 phase. They attributed this effect to redistribution of holes induced by pressure. Nelmes et al.$^7$ determined the crystal structure of the 124 phase...
under pressures up to 5 GPa and suggested that the reduction of the Cu(2)-O(1) distance, i.e. the
distance between the copper in the CuO₂ planes and the apical oxygen, with pressure gives rise to
increase in Tᵢ by the charge transfer mechanism. This suggests that the chemical substitution,
such as substitution of Sr²⁺ for Ba²⁺, that causes contraction of the lattice of the 124 phase along
the c-axis might shorten the Cu(2)-O(1) distance and, accordingly, increase Tᵢ of the 124 phase.

Miyatake et al. have shown that substitution of Ca for 10% of Y in the 124 phase raises Tᵢ up
to 90 K.⁸ They attributed the increase in Tᵢ to the increase in the hole concentration in the
CuO₂ planes. It would be interesting to know if there is a similar effect when monovalent
cations are substituted for Ba²⁺.

It is generally known that the synthesis of the 124 phase by solid-state reaction requires a
high oxygen pressure of 400 bar and a high temperature of 1040°C.⁴ Flux method,⁵ spray
drying⁶ or sol-gel technique,⁷ have recently been shown to enable the formation of the
124 phase under 1 atm oxygen at temperatures lower that 800°C. The present authors, in
fact, succeeded in preparing a single phase 124 by heating metal acetate-derived gels at 780°C
under 1 atm oxygen.¹²¹³ This suggests that the sol-gel technique has great advantage in
preparing a single 124 phase with partially substituted elements.

In this work, we tried to prepare YBa₂ₓRₓCu₄O₈ (R=Sr, K or Na) by the sol-gel method
and examined the changes in lattice constants, oxygen content, hole concentration, Tᵢ, and
microstructure with the Ba-site substitution. Substitution of Sr²⁺, which has a smaller ionic
radius than Ba²⁺, for Ba²⁺ was expected to shorten the lattice constant c. Substitution of K⁺,
which has a lower valence and a similar ionic radius, for Ba²⁺ was expected to increase the hole
concentration. Substitution of Na⁺, which has a smaller ionic radius and a lower valence, for
Ba²⁺ was expected to have both these effects.

2. EXPERIMENTAL PROCEDURE

Metal acetates Y(CH₃COO)₃·4H₂O (Mitsuwa Pure Chemicals, Osaka), Ba(CH₃COO)₂
(Wako Pure Chemicals, Osaka), Sr(CH₃COO)₂·0.5H₂O (Wako Pure Chemicals), CH₃COOK
(Nacalai Tesque, Kyoto), CH₃COONa·3H₂O (Nacalai Tesque) and Cu(CH₃COO)₂ (Wako
Pure Chemicals) were used as starting materials. Pertinent metal acetates were dissolved in ion-
exchanged water to make aqueous solutions with cation molar ratio of Y : Ba : R : Cu=1 : (2—x) :
x : 4 (R=Sr, K, Na; x=0~0.6). After stirring the solution for 1 h, an aqueous solution of tartaric acid (C₄H₆O₆) was added and the solution was stirred for 2 h. The molar ratio
tartaric acid to copper was fixed at C₄H₆O₆/Cu=0.43. The resultant transparent solution was
concentrated at 80°C in an oven, and a dried gel with blue color was obtained in three days. The
gel was pulverized, heated to 780°C at a rate of 160°C/h in flowing oxygen, kept there for 10 h and
cooled in the furnace. The resultant powder with black color was ground and heated at 780°C in
flowing oxygen for other 40 h with intermittent grinding every 10 h. The resultant powder
products were pressed into pellets and sintered at 780°C for 10 h in flowing oxygen for the
measurement of electrical resistance.

The crystalline phases in the products were identified by the powder x-ray diffraction (XRD)
method with a Rigaku Denki Company model RAD-IIA diffractometer using CuKα radiation.
The lattice constants of the 124 phase were determined by XRD using Si as the internal standard
substance. The d values were calculated from the measured 2θ values using the least square
The oxygen contents of the products were determined by an iodometric titration technique. First, for the determination of the content of copper in the product, the exactly weighed powder product ($W_1$ g) was dissolved in 1 N HCl, and KI and a buffer solution consisting of ammonium acetate and acetic acid were added to the solution. The resultant solution was titrated with a N/100 Na$_2$S$_2$O$_3$ standard solution ($V_1$ l) with bubbling N$_2$ using an aqueous solution of starch as an indicator. For the determination of the valence of copper represented by Cu$^{2+}$, the exactly weighed powder product ($W_2$ g) was dissolved in 1 N HCl solution to which KI was previously added, followed by an addition of the buffer solution. The resultant solution was titrated with the N/100 Na$_2$S$_2$O$_3$ standard solution ($V_2$ l). The formal charge of copper, 2+$\rho$, was determined from the following equation:

$$\rho = (V_2/W_2)/(V_1/W_1) - 1.$$ 

The oxygen content was calculated taking into account the balance of the positive and negative charge of the component ions in YBa$_{2-x}$R$_x$Cu$_4$O$_8$.

The potassium content of the product was determined by a flame spectrometrical analysis. The K-containing product was dissolved in 1 N HCl and diluted to make a solution with K$^+$ concentration of 0.1–1.0 ppm. The solution was analyzed by a spectrometrical method with a Seiko Instrument Company model SAS-727 atomic absorption spectrophotometer. The exact concentration of K$^+$ in the solution was determined from a calibration curve which was obtained by analysis of standard solutions of K$^+$ with a concentration of 0.1, 0.4, 0.7 and 1.0 ppm.

The d.c. electrical resistance of the sintered pellets was measured at temperatures from 300 K to 30 K by a four probe method with a Chino Instrument Company superconductivity test system. The cooling rate was fixed at 17 K/h.

The microstructure of the sintered pellets was observed with a Hitachi model S-450 scanning electron microscope (SEM).

### 3. RESULTS

#### 3.1 Formation of YBa$_{2-x}$R$_x$Cu$_4$O$_8$

The formation of substituted 124 crystalline products took place through the crystallization process similar to that for the formation of non-substituted YBa$_2$Cu$_4$O$_{8\delta}$, which was described previously. Figure 1 shows, for instance, the XRD patterns of the powder products obtained by heating the gel with a composition of YBa$_{1.8}$Sr$_{0.2}$Cu$_4$O$_8$ for 10, 30 and 50 h in flowing oxygen. CuO, Y$_2$Cu$_2$O$_5$, Ba$_2$Cu$_3$O$_{5+x}$ and Ba$_2$Cu$_3$O$_{5.9}$ remain in the sample in addition to the 124 phase after heating the gel at 780°C for 10 h. As the heating time increases, the amounts of impurity phases decrease and a single phase of YBa$_{1.8}$Sr$_{0.2}$Cu$_4$O$_8$ is obtained after heating for 50 h.

The XRD patterns of the products YBa$_{2-x}$Sr$_x$Cu$_4$O$_{8\delta}$, YBa$_{2-x}$K$_x$Cu$_4$O$_{6.8}$ and YBa$_{2-x}$Na$_x$Cu$_4$O$_{6.8}$ are shown in Fig. 2, 3 and 4, respectively. These figures indicate that a single phase is obtained for compositions up to $x=0.4$ for Sr, $x=0.2$ for K and $x=0.1$ for Na. For compositions of $x=0.6$ for Sr (Fig. 2), $x=0.3$ for K (Fig. 3) and $x=0.15$ and 0.2 for Na (Fig. 4), impurity phases such as Y$_2$Cu$_2$O$_5$, Ba$_2$Cu$_3$O$_{5.9}$, CuO, Y$_2$BaCuO$_5$ or unknown phases remain in the samples after heating for 50 h.

According to the flame spectrometric analysis, only 0.04 wt% decrease in the potassium content was observed.
content was observed after the heat-treatment both in YBa$_{1.9}$K$_{0.1}$Cu$_{4}$O$_{8}$ and YBa$_{1.8}$K$_{0.2}$Cu$_{4}$O$_{6.8}$. This confirms that the potassium remains in the sample in an amount corresponding to the starting composition.

3.2 Lattice Constants

The lattice constants of the 124 phases are shown in Table I and Fig. 5. The values of YBa$_2$Cu$_4$O$_8$ are $a=0.3846$, $b=0.3869$ and $c=2.723$ nm, which are in good agreement with the values determined with a neutron diffraction method by Lightfoot et al.\textsuperscript{14) Lattice constants $a$, $b$ and $c$ of Sr-124 phase decrease monotonically with increasing Sr concentration. In K-124 phase lattice constant $a$ slightly decreases with increasing K, and lattice constants $b$ and $c$ remain almost constant. In Na-124 phase lattice constant $a$ decreases with increasing Na, whereas $b$ and $c$ remain constant.
Effects of Substitution on the Structure and Properties of $\text{YBa}_2\text{Cu}_4\text{O}_8$

![Figure 3. The XRD patterns of $\text{YBa}_{2-x}\text{K}_x\text{Cu}_4\text{O}_8$ phases obtained by heating the gel at 780°C for 30-50 h in flowing oxygen.](image1)

![Figure 4. The XRD patterns of $\text{YBa}_{2-x}\text{Na}_x\text{Cu}_4\text{O}_8$ phases obtained by heating the gel at 780°C for 30-50 h in flowing oxygen.](image2)

### Table I. Lattice constants, oxygen content and superconducting transition temperature of Ba-site substituted $\text{YBa}_{2-x}\text{R}_x\text{Cu}_4\text{O}_6$ ($\text{R} = \text{Sr}, \text{K} \text{ or } \text{Na}$).

<table>
<thead>
<tr>
<th>$R_x$</th>
<th>Lattice constants/(\text{nm})</th>
<th>Oxygen content</th>
<th>$T_c$ (onset)/K</th>
<th>$T_c$ (end)/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>non-substituted</td>
<td>$a=0.3846$ $b=0.3869$ $c=2.7230$</td>
<td>$z=8.04$</td>
<td>87</td>
<td>74</td>
</tr>
<tr>
<td>$\text{Sr}_{0.2}$</td>
<td>$a=0.3837$ $b=0.3867$ $c=2.7208$</td>
<td>$z=7.98$</td>
<td>90</td>
<td>76</td>
</tr>
<tr>
<td>$\text{Sr}_{0.4}$</td>
<td>$a=0.3833$ $b=0.3863$ $c=2.7154$</td>
<td>$z=7.96$</td>
<td>90</td>
<td>72</td>
</tr>
<tr>
<td>$\text{Sr}_{0.6}$</td>
<td>$a=0.3830$ $b=0.3862$ $c=2.7144$</td>
<td></td>
<td>86</td>
<td>73</td>
</tr>
<tr>
<td>$\text{K}_{0.1}$</td>
<td>$a=0.3843$ $b=0.3871$ $c=2.7234$</td>
<td>$z=7.83$</td>
<td>86</td>
<td>73</td>
</tr>
<tr>
<td>$\text{K}_{0.2}$</td>
<td>$a=0.3842$ $b=0.3870$ $c=2.7228$</td>
<td>$z=7.71$</td>
<td>86</td>
<td>73</td>
</tr>
<tr>
<td>$\text{K}_{0.3}$</td>
<td>$a=0.3842$ $b=0.3871$ $c=2.7225$</td>
<td></td>
<td>87</td>
<td>78</td>
</tr>
<tr>
<td>$\text{Na}_{0.1}$</td>
<td>$a=0.3843$ $b=0.3868$ $c=2.7232$</td>
<td>$z=7.85$</td>
<td>87</td>
<td>78</td>
</tr>
<tr>
<td>$\text{Na}_{0.15}$</td>
<td>$a=0.3841$ $b=0.3868$ $c=2.7225$</td>
<td></td>
<td>85</td>
<td>78</td>
</tr>
<tr>
<td>$\text{Na}_{0.2}$</td>
<td>$a=0.3840$ $b=0.3869$ $c=2.7222$</td>
<td></td>
<td>85</td>
<td>78</td>
</tr>
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* Not a single phase of the 124.
3.3 Oxygen Content

The oxygen content of the single phase products are shown in Table I. The non-substituted YBa$_2$Cu$_4$O$_8$ sample has an oxygen content of 8.04. Sr-124 samples have oxygen contents of 7.98 for $x=0.2$ and 7.96 for $x=0.4$. All these values are close to stoichiometric value of 8. On the other hand, K-124 and Na-124 samples have oxygen contents of 7.83 and 7.71 for $x=0.1$ and 0.2 of K, respectively, and 7.85 for $x=0.1$ of Na, which are appreciably lower than 8. These values are lower than those calculated on the assumption that decrease in charge due to K$^+$ and Na$^+$
substitution is compensated by the formation of oxygen vacancies; the calculated values are 7.95 for \( x=0.1 \) and 7.90 for \( x=0.2 \).

### 3.4 Electrical Resistance

The temperature dependence of electrical resistance of the sintered pellets are shown in Fig. 6. All the samples show superconducting transition and metallic behavior of conduction above \( T_c \). Table I shows \( T_c \) (onset) and \( T_c \) (end) of the samples. Non-substituted 124 sample showed \( T_c \) (onset) of 87 K and \( T_c \) (end) of 74 K. Sr-124 phase of \( x=0.2 \) showed 3 K higher \( T_c \) (onset) and 2 K higher \( T_c \) (end) than those of non-substituted 124 phase, while Sr-124 phase of \( x=0.4 \) showed 2 K lower \( T_c \) (end). Sr-124 phase of \( x=0.6 \) containing impurity phases showed 3 K lower \( T_c \) (end). K-124 phase of \( x=0.1 \) and 0.2 showed 1 K lower \( T_c \) (onset) and \( T_c \) (end), while K-124 phase of \( x=0.3 \) with impurity phases showed the same \( T_c \) (end) as non-substituted 124 phase. Both Na-124 phases of \( x=0.1 \) (single phase) and 0.2 (not single phase) showed 4 K higher \( T_c \) (end) than non-substituted 124 phase.
3.5 SEM Observation

SEM photographs of sintered pellets of non-substituted 124 phase, Sr-124 phase of $x=0.4$, K-124 phase of $x=0.2$ and Na-124 phase of $x=0.1$ are shown in Fig. 7. It is seen that grains of K-124 and Na-124 phases are larger than those of non-substituted 124 and Sr-124 phases. The grain sizes are approximately 0.2–1.0 $\mu$m for non-substituted 124 and Sr-124 phases, and 1.0 $\mu$m for K-124 and Na-124 phases. It appears that K-124 and Na-124 pellets, which consist of plate-like grains, are sintered better than non-substituted 124 and Sr-124 pellets, which consist of smaller spherical grains.

4. DISCUSSION

4.1 Changes of Lattice Constants

There are three factors which determine the lattice constants of the present 124 phases; (1)
Effects of Substitution on the Structure and Properties of YBa$_2$Cu$_4$O$_8$

Ionic radii of Ba$^{2+}$, Sr$^{2+}$, K$^+$ and Na$^+$, (2) their valence and (3) oxygen vacancies. All the lattice constants $a$, $b$ and $c$ of Sr-124 phase decrease with increasing Sr concentration $x$. In the substitution of Sr for Ba, the valence of cations does not change and accordingly oxygen vacancies are not formed. Therefore, the changes of the lattice constants are caused by the difference of the ionic radius of Ba$^{2+}$ (0.152 nm) and that of Sr$^{2+}$ (0.136 nm). Since Sr$^{2+}$ ions are smaller, the introduction of Sr$^{2+}$ ions into Ba-site would contract the lattice. Fig. 5 shows that this is actually the case. It should be noted that a rate of contraction of $b$-axis with increasing $x$ is smaller than that of $a$-axis. This may result from the existence of double CuO chains along $b$-axis.

Lattice constant $a$ of K-124 phase slightly decreases with increasing K concentration, whereas $b$ and $c$ are constant. Since the ionic radii of Ba$^{2+}$ (0.152 nm) and K$^+$ (0.159 nm) are nearly the same, it is assumed that the difference in valence and the formation of oxygen vacancies affect the lattice constants as follows. In the 123 phase YBa$_2$Cu$_3$O$_{6.8}$, lattice constant $a$ increases and $b$ slightly decreases with increasing oxygen vacancies. As the oxygen content decreases, oxygen vacancies are formed on the O(4) site, i.e. on the CuO single chains along $b$-axis, and, at the same time, occupation of the chain sites along $a$-axis by oxygen takes place. This may be assumed to correspond to increase in lattice constant $a$ and slight decrease in $b$ with increasing oxygen vacancies in the 123 phase. In the 124 phase, however, it is thought that oxygen vacancies are less effective on changes of lattice constants, especially on $b$- and $c$-axis, than in the 123 phase because the number of oxygens in the chain site of the 124 phase is twice that of the 123 phase. In addition, the effect of one oxygen vacancy formed in one CuO chain in the 124 phase may be minimized by the presence of the adjacent CuO chain. These explain the negligible change in the lattice constants $b$ and $c$ in K-124 phase.

The slight decrease in $a$-axis in K-124 phase may result from the smaller electrostatic interaction between K$^+$ and the CuO$_2$ plane. Ba$^{2+}$ ions strongly interact with the CuO$_2$ plain with a negative charge and shift toward the plane in the direction of $c$-axis. Because of the smaller positive charge, the interaction of K$^+$ ions in the Ba-site with the CuO$_2$ plane may be weaker than Ba$^{2+}$ ions. This would cause a larger Cu(2)-O(2) interaction and hence smaller Cu(2)-O(2) distance, resulting in contraction of $a$-axis.

Lattice constant $a$ of Na-124 phase decreases with Na concentration, which is thought to be caused by the smaller ionic radius of Na$^+$ (0.124 nm) than that of Ba$^{2+}$ (0.152 nm). Lattice constants $b$ and $c$ of Na-124 phase remain almost unchanged with increasing Na concentration. It may be possible that the maximum content of Na$^+$ that forms the single phase 124, $x=0.1$ in the present case, is so low that the change in lattice constants $b$ and $c$ with the Na concentration might not be detected; the rate of change in the lattice constants $b$ in Sr-124 phase is, in fact, as small as that in Na-124 phase in the range of $x=0-0.2$ (see Fig. 5 (b)).

4.2 Effects of Substitution on $T_c$

We have attempted to change the lattice constants and introduce additional holes by substituting Sr$^{2+}$, K$^+$ or Na$^+$ for Ba$^{2+}$ in YBa$_2$Cu$_4$O$_8$. It was observed that the contraction of the lattice, especially those along $a$- and $b$-axes for the substitution of Sr$^{2+}$ and Na$^+$, increases $T_c$, although substitution of Sr$^{2+}$ in a large amount of $x=0.4$ results in a decrease in $T_c$. In oxide superconductors in which carriers are holes, a decrease in the bond length of Cu-O in the CuO$_2$ plane often raises the $T_c$. Since the high-$T_c$ superconductivity in cuprate superconductors is
based upon the hybrid of Cu 3d and O 2p orbitals in the two-dimensionally linked [CuO₂]∞, the
Cu-O bond length would affect the electronic structure and hence $T_c$. When the Cu-O distance
in the plane decreases, the overlap of Cu 3dₓ²₋₃ᵧ² and O 2pₓ orbitals may become larger and the
density of carriers may increase. In fact, Liu et al. found an increase in $T_c$ with decreasing
lattice constants $a$ and $b$ in rare-earth substituted 124 phases.

In contrast to the effect of the lattice constant $a$ and $b$ on $T_c$, the effect of the lattice constant $c$
is controversial. In discussing the physical pressure effect, it was shown that $T_c$ of the 124 phase
increases in proportion to decrease in the lattice constant $c$ because of the redistribution of holes
between the CuO chains and the CuO₂ planes, which is caused by the shortening of Cu(2)-O(1)
distance. Wada et al., however, synthesized Sr-substituted 124 phase under high oxygen
pressure, reporting that the change in $T_c$ with increasing Sr content or decreasing lattice constant
$c$ is negligible. Lately, Ishigaki et al. claimed that the distribution of holes in the Sr-
substituted 124 phase is essentially the same as the non-substituted 124 phase at 0 GPa on the
basis of the calculation of Madelung energy, taking account of the displacement not only of Cu(2)
and O(1) but also of all other ions by Sr substitution.

Although the changes in $T_c$ with the substitution observed in the present study are not quite
large, substitution of smaller cations for Ba²⁺ is likely to increase $T_c$ through decreasing the
lattice constants $a$ and $b$. This was confirmed by substituting three kinds of cations, Sr²⁺, K⁺
and Na⁺, two of which have smaller ionic radii than Ba²⁺ and one has almost the same ionic
radius as Ba²⁺. Since the smaller change in the lattice constant $c$ than $a$ was observed,
especially in the range of $x=0—0.2$, it can be concluded that the increase in $T_c$ is caused by the
contraction of the CuO₂ plane in the present substitution.

The expected increase in $T_c$ (onset) was not observed in the K- or Na-124 phases. It is
thought that substitution of alkali cations in the present work is not effective to increase holes in
the CuO₂ planes because the oxygen vacancies are formed for the charge compensation. On the
other hand, grain growth of the polycrystalline 124 phases was promoted by substitution of alkali
cations; that is, the grain size increases and the shape of grains changes from particle to plate like
ones. Therefore, in the Na⁺-substituted sample, YBa₁.₉Na₀.₁Cu₄O₇.₈₅, the increase in $T_c$ (end)
by 4 K may result from the decrease in the weak link of grain boundaries rather than the effect of
the lattice contraction.

5. CONCLUSION

Single-phase YBa₂₋ₓRxCu₄O₈ (R=Sr, K, Na) superconductors were successfully prepared
by the sol-gel method under ambient pressure, and the effects of the partial substitution of Sr²⁺,
K⁺ or Na⁺ for Ba²⁺ on the structure and properties of YBa₂Cu₄O₈ were investigated.

(1) The lattice constants $a$, $b$ and $c$ of the 124 phase monotonically decreased with
substitution of Sr for Ba. The slight increase in $T_c$ (onset) and $T_c$ (end) observed at $x=0.2$ was
attributed to the lattice contraction in the CuO₂ plane.

(2) The lattice constant $a$ of the 124 phase slightly decreased and $b$ and $c$ did not change with
substitution of K. The oxygen content decreased and $T_c$ hardly changed with substitution of K.
An expected increase in $T_c$ by hole doping could not be achieved because the charge
compensation was not made by the formation of holes but by the formation of oxygen vacancies.

(3) The lattice constant $a$ of the 124 phase decreased and $b$ and $c$ did not change with
substitution of Na for Ba. The oxygen content decreased and $T_c$ (onset) hardly changed with substitution of Na as in the case of that of K. $T_c$ (end), however, rose by 4 K on substitution of Na for Ba, probably due to the lattice contraction in the CuO$_2$ plane and/or the decrease in the weak link of grain boundaries.

(4) Grain growth and change in the shape of the grains from particulate to plate-like ones were observed in the K- and Na-substituted 124 samples.

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