Effect of co-substitution on superconductivity in (Y,Ca)(Ba,Sr)$_2$Cu$_4$O$_8$ prepared by the molten KOH method

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Abstract. Effect of co-substitution of Ca and Sr in the Y-124 phase of Y$_{1-x}$Ca$_x$Ba$_2$Sr$_2$Cu$_4$O$_8$ has been investigated. Polycrystalline samples of Y$_{1-x}$Ca$_x$Ba$_2$Sr$_2$Cu$_4$O$_8$ with 0 ≤ x(Ca) ≤ 0.2 and 0 ≤ y(Sr) ≤ 0.2 have been prepared by the molten KOH method. The lattice parameters decrease with increasing y(Sr), indicating that the smaller Sr ions are systematically substituted for the larger Ba ions. The value of $T_c$ increases from 83 K to ~ 90 K through the Sr-substitution for x(Ca) = 0, while $T_c$ ~ 90 K are almost independent of y(Sr) for x(Ca) = 0.1 and 0.2.

1. Introduction
Among numerous high-$T_c$ superconducting cuprates, the so-called RE-123 system of REBa$_2$Cu$_3$O$_7$ (RE = rare-earth elements) with the superconducting transition temperature $T_c$ ~ 90 K is superior to the other superconductors in superconducting properties in a magnetic field and is expected to be applied to high-magnetic-field apparatus such as nuclear magnetic resonance (NMR) spectrometers, magnetic resonance imaging (MRI) machines, and accelerators. For such large-scale practical applications, there is an important issue to be resolved that both its critical current density $J_c$ and irreversibility field $B_I$ are still too low at liquid nitrogen temperature 77 K. The introduction of artificial nanoscale defects for the enhancement of flux pinning in RE-123 films has been proven to be a powerful method to increase $J_c$ and $B_I$. Another effective way to increase $J_c$ and $B_I$ is to increase $T_c$. Although the increase in $T_c$ by at least 5–10 K is desired, it has been extremely hard to realize so far.

The cuprate superconductor REBa$_2$Cu$_3$O$_7$ (RE-124) has a similar crystal structure to RE-123. RE-124 contains the double chains of edge-sharing [CuO$_2$] squares instead of the single chain of corner-sharing ones in RE-123. Since the double chains in RE-124 are leading to its thermal stability and rigorous oxygen stoichiometry, RE-124 is a more promising candidate for practical applications than RE-123. $T_c$ ~ 80 K of Y-124 [1] is lower than 92 K of Y-123 and too low for practical applications at liquid nitrogen temperature. However, $T_c$ of Y-124 has been reported to greatly enhanced up to 108 K by applying a high pressure of 12 GPa [6] in contrast to RE-123 in which $T_c$ hardly changes under high pressure [7,8], indicating that Y-124 has a potential of high $T_c$ above 100 K.

The reason for the relatively low $T_c$ of Y-124 is due to the low hole-concentration in the conducting CuO$_2$ plane. Kaldis et al. [9] have claimed that hole-transfer from the double chains to the CuO$_2$ plane occurs due to the decrease in the distance between Cu in the CuO$_2$ plane and apical O under high pressure. In the case of application of chemical pressure through the partial substitution of 30% Sr$^{2+}$ for Ba$^{2+}$ in Y(Ba,Sr)$_2$Cu$_4$O$_8$, actually, Miyachi et al. [10] has reported that $T_c$ increases up to 90 K, whereas there have been several reports that $T_c$ decreases or increases slightly through the Sr-substitution [11-13]. In
the case of hole-doping into the CuO$_2$ planes through the partial substitution of 10–20% Ca$^{2+}$ for Y$^{3+}$ in (Y,Ca)Ba$_2$Cu$_3$O$_6$ [2-5], on the other hand, its $T_c$ has been increased up to 90 K by increasing the hole concentration. Accordingly, $T_c$ is expected to increase further by both the method of the increase of the hole concentration in the CuO$_2$ planes through chemical pressure through the Sr$^{2+}$-substitution for Ba$^{2+}$ and the hole-doing through the Ca$^{2+}$-substitution for Y$^{3+}$. In this study, we have investigated the effects of co-substitution of Ca for Y and Sr for Ba in Y$_{1-x}$Ca$_x$Ba$_{2-y}$Sr$_y$Cu$_4$O$_8$ to explore the possibility of $T_c$ above 100 K at ambient pressure.

2. Experimental

Samples of Y$_{1-x}$Ca$_x$Ba$_{2-y}$Sr$_y$Cu$_4$O$_8$ (0 ≤ x(Ca) ≤ 0.2, 0 ≤ y(Sr) ≤ 0.2) were prepared by a molten KOH method, which was widely used in previous studies of RE-124 phase [10, 14-19]. Starting materials were powders of Y$_2$O$_3$, CuO, BaO$_2$, SrCO$_3$ and CuO. The powders weighted stoichiometrically were mixed and put in an alumina crucible together with KOH to the starting materials. Typical amount were 4g of KOH and 2 g of the powder for Y$_{1-x}$Ca$_x$Ba$_{2-y}$Sr$_y$Cu$_4$O$_8$. The crucible was heated to 650˚C at 2˚C/min and kept for 24 h in air. The melt was cooled to room temperature for about 3 h in the furnace. Black tiny crystals precipitated on the bottom of the crucible were isolated by dissolving KOH with distilled water and methanol and then dried at 150˚C in air. The structural analysis was carried out by the powder x-ray diffraction using Cu Ka radiation to determine the lattice parameters. Magnetic susceptibility measurements were performed using a SQUID magnetometer to determine $T_c$.

3. Results

Figure 1 shows the powder x-ray diffraction patterns for selected samples of co-substituted Y$_{1-x}$Ca$_x$Ba$_{2-y}$Sr$_y$Cu$_4$O$_8$. The obtained samples contain the Y-124 phase as a main phase, although impurity phases such as Y$_2$Cu$_2$O$_5$, CuO and Y$_2$O$_3$, which are often observed in the samples prepared by the molten KOH method [10,14,15], are included.

![Figure 1](image-url)
Figure 2 shows the $y$(Sr)-dependence of lattice parameters for $Y_{1-x}$Ca$_{x}$Ba$_{2-y}$Sr$_{y}$Cu$_4$O$_8$ with $x$(Ca) = 0, 0.1, and 0.2. It is found that $a$-, $b$-, and $c$-axis lengths tend to decrease with increasing $y$(Sr) for all $x$(Ca) and that the $c$-axis length increases with increasing $x$(Ca) for all $y$(Sr). These results indicate that the systematically co-substituted samples are obtained, although the chemical analysis is necessary to determine the actual composition.

Figure 2. Dependences of the lattice parameters on the Sr-content $y$(Sr) for $Y_{1-x}$Ca$_{x}$Ba$_{2-y}$Sr$_{y}$Cu$_4$O$_8$ with (a) $x$(Ca) = 0, (b) $x$(Ca) = 0.1 and (c) $x$(Ca) = 0.2, where $x$(Ca) and $y$(Sr) are nominal values.

Figure 3 shows the temperature dependence of the magnetic susceptibility $\chi$ in a magnetic field of 10 Oe on warming after zero-field cooling for $Y_{1-x}$Ca$_{x}$Ba$_{2-y}$Sr$_{y}$Cu$_4$O$_8$. A single-step diamagnetic signal due to the shielding effect is observed for all samples. The superconducting volume fraction estimated from the shielding signal at 20 K is about 50–90%, indicating the appearance of bulk superconductivity.

Figure 3. Temperature dependence of the magnetic susceptibility $\chi$ and that around $T_c$ for $Y_{1-x}$Ca$_{x}$Ba$_{2-y}$Sr$_{y}$Cu$_4$O$_8$ with (a) $x$(Ca) = 0, (b) $x$(Ca) = 0.1 and (c) $x$(Ca) = 0.2, where $x$(Ca) and $y$(Sr) are nominal values.
The value of $T_c$ is defined as the onset temperature of the shielding effect. The $y$(Sr)-dependences of $T_c$ for $x$(Ca) = 0, 0.1, and 0.2 are shown in figure 4. As for $x$(Ca) = 0, $T_c$ = 83 K for $y$(Sr) = 0 increases up to 91 K for $y$(Sr) = 0.2. This result is in good agreement with that in the previous study of YBa$_2$$_3$ Sr,Cu$_4$O$_8$ prepared by the molten KOH method [10]. One possible explanation of this enhancement of $T_c$ is due to the fact that the hole concentration increases in the CuO$_2$ plane and decreases in the Cu-O double chains by the chemical pressure through the Sr-substitution for Ba as reported in the high-pressure study of Y-124 by Kaldis et al. [9]. Another possible explanation is due to the increase in the hole concentration in the CuO$_2$ plane by substituting Y$^{3+}$ with Sr$^{2+}$ as pointed out by Miyachi et al. [10]. As for $x$(Ca) = 0.1 and 0.2, the value of $T_c$ ~91–92 K for $y$(Sr) = 0 is in good agreement with that in the previous studies of Y$_{1-x}$Ca$_x$Ba$_2$Sr$_2$Cu$_4$O$_8$ prepared by several methods [2-5]. This increase in $T_c$ through the Cu$_{2+}$-substitution for Y$^{3+}$ is due to the increase in the hole concentration in the CuO$_2$ plane. Notice that $T_c$ ~ 90 K is almost constant or tends to decrease very slightly with increasing $y$(Sr) for $x$(Ca) = 0.1 and 0.2. One possible explanation is as follows: holes transfer from the double chains to the CuO$_2$ planes by the chemical pressure through the Sr-substitution in the case of $x$(Ca) = 0 with the insufficient hole-concentration in the CuO$_2$ plane, while such hole-transfer no longer occur in the case of $x$(Ca) = 0.1 and 0.2 with the sufficient hole-concentration in the CuO$_2$ plane. Moreover, the slight decrease in $T_c$ with the increase in $y$(Sr) may be due to the disorder caused by the Sr/Ba-substitution. Another possible explanation is that hole-transfer occurs by both Ca- and Sr-substitutions and the slight decrease in $T_c$ through the Sr-substitution observed for the Ca-substituted samples is due to the overdoping of holes in the CuO$_2$ plane. In any case, the determination of hole concentration in the CuO$_2$ plane is required to understand this behavior.

4. Conclusions
We have investigated the possibility of $T_c$ above 100 K at ambient pressure in the Y-124 phase by both the hole-doping through the Ca-substitution for Y and the chemical pressure through the Sr-substitution for Ba. Polycrystalline samples of Y$_{1-x}$Ca$_x$Ba$_2$$_3$Sr$_2$Cu$_4$O$_8$ with 0 ≤ $x$(Ca) ≤ 0.2 and 0 ≤ $y$(Sr) ≤ 0.2 have been prepared by the molten KOH method. It has been found from the variations of the lattice parameters
that co-substituted samples are successfully obtained. It has been also found that $T_c \sim 90$ K is almost constant through the Sr-substitution in the Ca-substituted samples. Therefore, it appears that $T_c \sim 90$ K is the upper limit at ambient pressure in $Y_{1-x}Ca_xBa_{2-y}Sr_yCu_4O_8$. To clarify why $T_c$ does not increase up to 100 K, the further research, including the measurement of hole concentration in the CuO$_2$ plane, is necessary.

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