# BRIEF COMMUNICATION

# Strontium Substitution in Superconducting $R$Ba$_2$Cu$_4$O$_8$ ($R$=Gd and Ho) Compound

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The effect of substitution of Sr for a part of Ba in superconducting GdBa$_2$Cu$_4$O$_8$ and HoBa$_2$Cu$_4$O$_8$ on critical temperatures and lattice constants was investigated. The critical temperatures were definitely unchanged in spite of the reduction of the unit cell which was reportedly effective for the enhancement of the critical temperature in the rare-earth element substitution. The orthorhombicities of unit cells increased with the Sr content, as resulted from the large shortening of the $a$ axis compared with the $b$ axis. In the present work, the dependence of the shortening of each axis on the ionic radius of a rare-earth element was found. © 1997 Academic Press

## 1. INTRODUCTION

The rare-earth element (denoted $R$) has played a significant role in the superconducting $R$Ba$_2$Cu$_4$O$_8$ compound (called 124), which is in the neighborhood of CuO$_2$ planes where superconduction is expected to occur. The critical temperature ($T_c$) of 124 varied with the ionic radius of $R$ ($r_R$) (1, 2); The $T_c$ monotonically increased with a decrease in $r_R$. Since a smaller $R$ reduced the unit cell of 124, it has been considered that a smaller unit cell enhances the $T_c$ of 124.

The unit cells were reduced under high pressure (3–7). The $T_c$ was expectedly enhanced with increased pressure. Recently, the difference in the pressure dependence of $T_c$ on

$R$ was found (8), coming from the behavior in the reduction of unit cell. GdBa$_2$Cu$_4$O$_8$ (Gd124) showed strong dependence compared with YBa$_2$Cu$_4$O$_8$ (Y124); Gd is a larger element than $Y$. It seems that the shortening of a large unit cell is much larger than that of a small unit cell under the same applied pressure.

Strontium was substituted for a part of Ba in 124 in order to make the reduced unit cell. It has been reported that the $T_c$'s of Sr-substituted Y124 and YbBa$_2$Cu$_4$O$_8$ (Yb124) were apparently unchanged (9, 10), although the Sr substitution has been regarded as applying a chemical pressure. Yb is the smallest element in $R$ for 124, for Lu-containing 124 has not yet been synthesized. On the other hand, the substitution effect of Sr for large $R$ such as Gd which can offer a large unit cell still remains unknown. The effective reduction for $T_c$ in the unit cell might be expected in Gd124 rather than in Y124 and Yb124 based on the strong pressure dependence of $T_c$ in the former (8).

The main purpose of the present work is to clarify the effect of $r_R$ on the $T_c$ and structural changes in the partly Sr-substituted 124. We investigated the $T_c$'s and lattice constants of Sr-substituted Gd124 and HoBa$_2$Cu$_4$O$_8$ (Ho124) comparable to Y124 in unit cell volume.

## 2. EXPERIMENTAL

Powders with compositions of Gd(Sr$_x$Ba$_{1-x}$)$_2$Cu$_4$O$_8$ and Ho(Sr$_x$Ba$_{1-x}$)$_2$Cu$_4$O$_8$ were prepared through spray-frozen/freeze-drying of aqueous solutions according to a previous report (11). The powders were pressed in disks and sintered at 1073 K under flowing oxygen. The sintering was

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carried out until XRD analysis confirmed the specimens to be of single 124 phase. The sintering time for single phase was prolonged with the Sr content. The single phase was accomplished with $x$ up to 0.1 for Gd124 and 0.3 for Ho124. The detailed preparation procedure was described elsewhere (11).

Lattice constants were estimated from least-squares fits using peaks with a scan speed of $0.1°$/min. Silicon powders were used as a standard. Resistivity and inductance measurements were performed to estimate the $T_c$. The resistivity was measured employing a standard four-probe method under constant current density of $0.05 \, A/cm^2$. Gold films for an electrode were deposited on the surfaces of specimens to make ohmic contact. Temperature was monitored by a Au(Fe)–Chromel thermocouple. The inductance was measured using the powdered specimens.

## 3. RESULTS AND DISCUSSION

It was confirmed that both the lattice constants of Gd124 and Ho124 linearly decreased with increased Sr content. This is due to the incorporation of smaller Sr into the Ba site. Table 1 shows the unit cell volumes calculated from the lattice constants obtained. The unit cell volumes for $x = 0$ in Gd124 and Ho124 were in agreement with the values in previous reports using high oxygen pressure in the preparation (1). For $x = 0.1$, Gd124 and Ho124 had unit cell volumes comparable to Tm124 with $T_c$ of ca. 82 K and to Dy124 with $T_c$ of ca. 76 K, respectively. The increase in orthorhombicity of the unit cell with the Sr content was marked. The values estimated by $b/a$ are shown in Table 1. According to the report by Moriss *et al.* (1), a large orthorhombicity appears in a small unit cell. Our results are consistent with their results. The value of orthorhombicity in Ho124 was more than 1.01 when the Sr content was above 0.2. Such large orthorhombicities were confirmed in the Sr substitution (9, 10), but not in the $R$ substitution (1, 2).

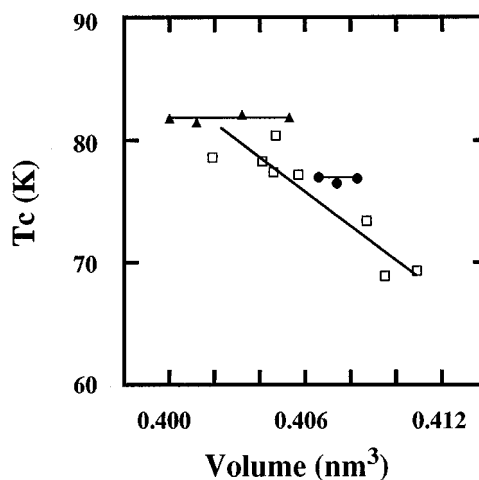Figure 1 represents the relationship between the $T_c$ and the unit cell volume in the Sr substitution. For comparison,



**FIG. 1.** Relationships between critical temperature ($T_c$) and unit cell volume. The solid circles and triangles show the data for $Gd(Sr_xBa_{1-x})_2Cu_4O_8$ and $Ho(Sr_xBa_{1-x})_2Cu_4O_8$ in the present work, respectively. The open squares show the data in the rare-earth element substitution reported previously (1).

the relationship in the $R$ substitution is shown. The $T_c$'s of Sr-substituted Gd124 and Ho124 were unchanged in spite of the reduction of the unit cell which has brought about the enhancement of $T_c$ in the $R$ substitution. Since these results are similar to those of Y124 (4) and Yb124 (5), it is considered that the behavior of $T_c$ in the Sr substitution does not vary with $r_R$. One group has claimed the enhancement of $T_c$ by Sr substitution (12), and observed two diamagnetic signals in the temperature dependence of magnetization for the Sr-substituted Y124: One was a very small signal around 90 K and the other was a large signal around 85 K at which pure Y124 exhibited the diamagnetic signal. However, if the $T_c$ of Y124 had been enhanced to 90 K by Sr substitution, a large diamagnetic signal should have been observed around 90 K, coming from the whole of specimen. Therefore, it is judged that their specimens contain a small amount of 123 phase with $T_c$ of 90 K as an impurity.

The difference between the Sr and $R$ substitution in the behavior of $T_c$ is obvious. According to the report by Zhang *et al.* (13), the divalent Sr ion preferentially occupies the Ba site rather than the $R$ site: the Sr and $R$ sites are $(1/2, 1/2, z)$ and $(1/2, 1/2, 0)$ in the space group $Ammm$, respectively (14). The Sr site is coordinated with 10 oxygen ions and the $R$ site with 8. It is clear that the positional difference of the incorporated element is responsible for the behavior of $T_c$. Mori *et al.* recently reported that the enhancement of $T_c$ in the $R$ substitution results from the shortening of the Cu–O length in the $CuO_2$ planes (2). However, since the shortening of the Cu–O length has been observed in the Sr-substituted Y124 (15), further structural investigation is needed to understand the difference in the behavior of $T_c$ in Fig. 1.

**TABLE 1**
**Changes in Volumes and Orthorhombicities of Unit Cells in $Gd(Sr_xBa_{1-x})_2Cu_4O_8$ and $Ho(Sr_xBa_{1-x})_2Cu_4O_8$ with Sr Content**

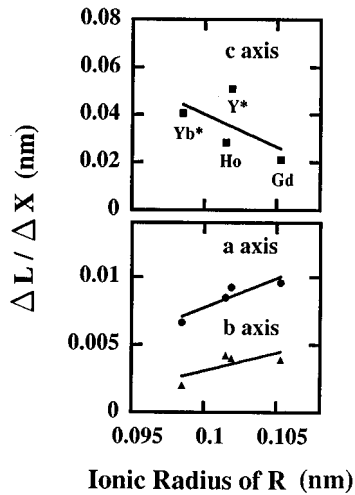|  | $Gd(Sr_xBa_{1-x})_2Cu_4O_8$ | | $Ho(Sr_xBa_{1-x})_2Cu_4O_8$ | |
|---|---|---|---|---|
| $X$ | Volume ($nm^3$) | $b/a$ | Volume ($nm^3$) | $b/a$ |
| 0 | 0.4083 | 1.0053 | 0.4053 | 1.0078 |
| 0.05 | 0.4074 | 1.0061 | | |
| 0.1 | 0.4066 | 1.0068 | 0.4032 | 1.0091 |
| 0.2 | | | 0.4012 | 1.0111 |
| 0.3 | | | 0.4000 | 1.0112 |

**FIG. 2.** Relationships between ionic radius of rare-earth element (*R*) (16) and shortening of each axis per composition parameter of Sr, *x*. The *L* on vertical axis represents lattice constant. The data for Y and Yb labeled with asterisks (∗) were estimated from the reports by Wada *et al.* (9) and Yaegashi *et al.* (10), respectively.

The present work found that the shortenings of the *a* and *b* axes of Gd124 were larger than those of Ho124 under the same Sr content, while the *c* axis was less shortened. The shortening of each axis in Ho124 was almost equal to that in Y124. The relationships between $r_R$ and the shortening of each axis per the composition parameter of Sr, *x*, are represented in Fig. 2. The shortening rate (expressed as $\Delta L/\Delta x$ in Fig. 2) of *a* and *b* axes increased with an increase in $r_R$, indicating that the change of *a*–*b* plane in large 124 such as Gd124 is large. The $\Delta L/\Delta x$ of the *b* axis was low compared to that of the *a* axis. This must be attributed to the double chain structure of CuO along its axis. From the results, it is understood that the shortening of the *a* axis is responsible for the large orthorhombic change. On the other hand, the substitution effect of Sr was greater along the *c* axis than along the *a* and *b* axes. The $\Delta L/\Delta x$ of the *c* axis was much higher than those of the *a* and *b* axes. The ionic radius

dependence of shortening for the *c* axis was opposite to those for the *a* and *b* axes; the $\Delta L/\Delta x$ of the *c* axis decreased with increasing $r_R$. In Table 2, the values of those shortening rates are summarized.

## 4. CONCLUSIONS

In the present work, we have recognized that the roles of *R* in 124 are significant for the structural changes in Sr substitution, but not for the $T_c$. Unlike *R* substitution, the $T_c$'s of Sr-substituted Gd124 and Ho124, as well as Y124, were definitely unchanged in spite of the reduction of the unit cell. The shortening behavior of each axis in the Sr substitution was strongly dependent on $r_R$; the $\Delta L/\Delta x$ of the *a* and *b* axes increased with increasing $r_R$, while that of the *c* axis decreased. The orthorhombicity of unit cell increased with the Sr content. This was due to the larger shortening of the *a* axis.

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**TABLE 2**
**Shortening Rates of the *a*, *b*, and *c* Axes of Sr-Substituted $RBa_2Cu_4O_8$ (*R* = Yb, Ho, Y, and Gd) Shown in Fig. 2**

| *R* | Ionic radius (nm) | $\Delta a/\Delta x$ (nm) | $\Delta b/\Delta x$ (nm) | $\Delta c/\Delta x$ (nm) |
|---|---|---|---|---|
| Yb | 0.0985 | 0.0067 | 0.0020 | 0.0406 |
| Ho | 0.1015 | 0.0085 | 0.0042 | 0.0283 |
| Y | 0.1019 | 0.0093 | 0.0040 | 0.0508 |
| Gd | 0.1053 | 0.0096 | 0.0039 | 0.0210 |