

## Effect of Gd Substitution for the Ca Site in the $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{1.91}$ $(\text{Ca}_{1-x}\text{Gd}_x)_{2.03}\text{Cu}_{3.06}\text{O}_{10+\delta}$ ( $x=0.0\sim 0.06$ ) Superconductors

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### ABSTRACT

The effect of substitution of Gd ions for Ca ions in the  $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{1.91}(\text{Ca}_{1-x}\text{Gd}_x)_{2.03}\text{Cu}_{3.06}\text{O}_{10+\delta}$  ( $x=0.0\sim 0.06$ ) was investigated by measuring x-ray diffraction patterns, lattice constants, dc resistivity and Hall effect. We found the solubility limit of Gd in the 110 K phase to be  $x < 0.015$ . Within the solubility limit, the *c*-axis seemed to decrease with increasing *x*. In the region of the 110 K single phase, the critical temperature  $T_c$  gradually decreased with an increasing the Gd concentration *x*, corresponding to a small change of the carrier concentration.

**Key words :** Bi(Pb)-Sr-Ca-Cu-O, Gd substitution for Ca, 110 K volume fraction

### 1. Introduction

Since the discovery of Bi-Sr-Ca-Cu-O superconductors by Maeda,<sup>1)</sup> many studies for the structure of these superconductors have been carried out. The results have consistently suggested that the Bi-Sr-Ca-Cu-O superconductors have three phases with Cu-O plane of perovskite structure.<sup>2,3)</sup> The three phases of Bi-superconductors are divided into the  $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+\delta}$  (10 K phase, 2201 phase), the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  (80 K phase, 2212 phase), and  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$  (110 K phase, 2223 phase) according to the critical temperature ( $T_c$ ) and the ratio of composition atoms.<sup>4-6)</sup>

The conduction mechanism in high- $T_c$  superconductors was related to the Cu-O plane of perovskite structure. Consequently, many studies have been done on the electronic structure of the Cu-O plane.<sup>7-12)</sup> As a result of replacement and substitution experiments in the superconductor structure, it is well known that in the high- $T_c$  superconductors<sup>13-19)</sup> there is a strong relationship between carrier concentration and transition temperature. The transition temperature ( $T_c$ ) increases with increasing carrier concentration until it passes through a maximum, after which it decreases, and becomes zero above a critical concentration.<sup>20)</sup> Thus, control of the hole concentration in the Cu-O plane is worth considering in order to elucidate the superconductivity mechanism of high- $T_c$  superconductors. The carrier concentration in the high- $T_c$  system may differ by varying the dopant and oxygen contents.

During the heating cycle, however, the oxygen deficiency is very small in the Bi-Sr-Ca-Cu-O system. Needless to say,

it is expected that the Bi-Sr-Ca-Cu-O system would be a more appropriate candidate for study in substitution experiments. Consequently, many groups have reported that in the 80 K phase of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  superconductors, the substitution of trivalent Y and other elements with different valence, for the divalent Ca, causes a drastic decrease in the carrier concentration. Furthermore, a transition from superconductor to insulator occurs due to the decrease in carrier concentration.<sup>21-27)</sup> In the 110 K phase, however, there have been few reports to test the effect of carrier concentration on the superconducting properties using substitution at the Ca site. Since the 110 K phase originally experiences substitution of Pb for Bi, it is very complicated to investigate the effects of substitution of other elements.<sup>28,29)</sup> Moreover, the 110 K phase very easily nucleates the 80 K phase, or other impurity phases, by small amounts of substitution.

In this present work, we have studied the substitution of trivalent Gd ions for the divalent Ca ions in the 110 K phase of a (Bi,Pb)-Sr-Ca-Cu-O superconductor. We have particularly focused on the solubility limit of Gd of the 110 K phase and the superconducting properties.

### 2. Experimental Procedure

Samples were prepared by the solid-state reaction method. The initial composition had a small excess of Ca and Cu and a small deficiency of Sr, compared to the stoichiometric ratio 2223. The nominal composition of the sample was  $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{1.91}(\text{Ca}_{1-x}\text{Gd}_x)_{2.03}\text{Cu}_{3.06}\text{O}_{10+\delta}$  ( $x=0\sim 0.06$ ), prepared from powders of  $\text{Bi}_2\text{O}_3$  (99.99%), PbO (99.99%),  $\text{SrCO}_3$  (99.99%),  $\text{CaCO}_3$  (99.99%),  $\text{Gd}_2\text{O}_3$  (99.99%), and CuO (99.99%). The pellets were pre-sintered at 830°C for 12 h in air and cooled to room temperature in the furnace. Then, they were pulverized, mixed, and pressed into pellets again.

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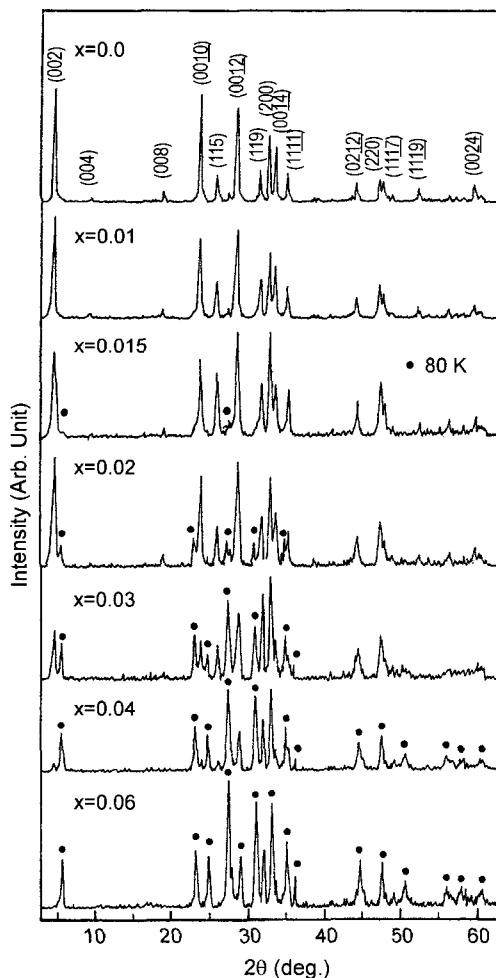
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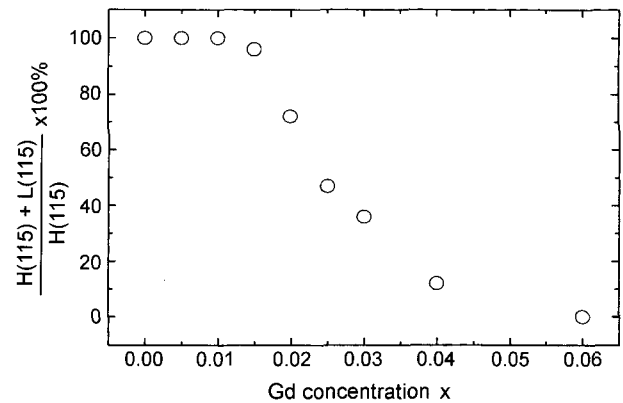
Finally, they were sintered at 857 to 860°C for 110 h in air, then cooled to room temperature in the furnace. The samples were analysed by x-ray powder diffraction method using CuK $\alpha$  radiation. Lattice parameter was refined using least square program by Cohens method. The resistivity of the samples was measured by the standard dc four-probe method using indium solder, and the Hall measurement was performed at room temperature by Van der Pauw method.

### 3. Results and Discussion

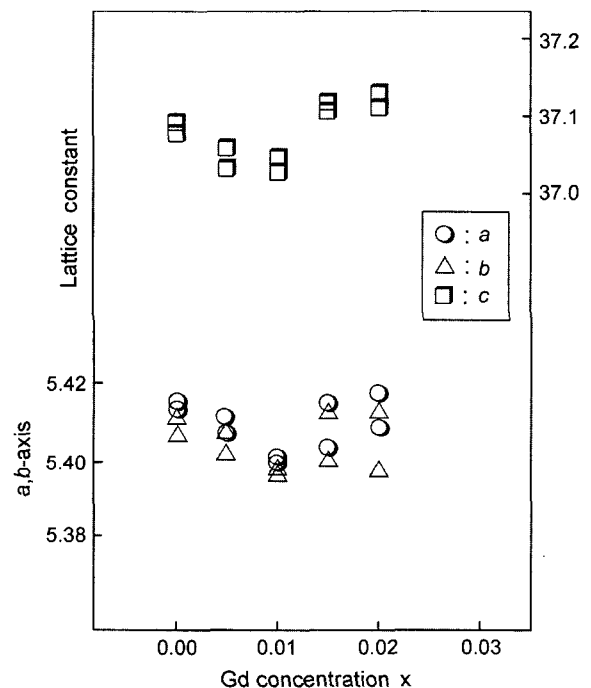
Fig. 1 shows the X-ray powder diffraction patterns for samples with various Gd concentrations  $x=0.0\sim 0.06$ . This figure indicates that the single phase was obtained below  $x < 0.015$ . In the range of  $x \geq 0.015$ , the peak intensity of the 80 K phase begins to increase at the expense of the 110 K phase. The 110 K phase almost disappears around  $x=0.06$ . From this figure, we conclude that the critical Gd concentration for the 110 K single phase exists for  $x < 0.015$ .



**Fig. 1.** The X-ray powder diffraction patterns of  $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{1.91}(\text{Ca}_{1-x}\text{Gd}_x)_{2.03}\text{Cu}_{3.06}\text{O}_{10+x}$  ( $x=0.0\sim 0.06$ ). For the sample with  $x=0.0$ , all peaks are indexed to the 110 K phase (● denotes the peaks of 80 K phase).



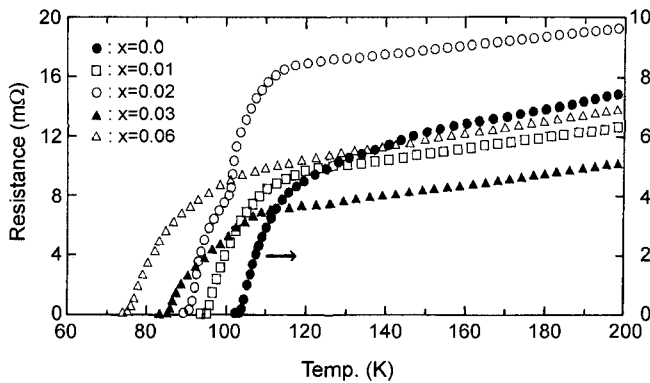
**Fig. 2.** The fractional intensity of 110 K phase in the  $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{1.91}(\text{Ca}_{1-x}\text{Gd}_x)_{2.03}\text{Cu}_{3.06}\text{O}_{10+x}$  ( $x=0.0\sim 0.06$ ) shown in Fig. 1.  $I(115)_H$  and  $I(115)_L$  mean the intensities of the (115) peaks of the 110 K and 80 K phases, respectively.



**Fig. 3.** Gd concentration dependence of lattice constants in  $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{1.91}(\text{Ca}_{1-x}\text{Gd}_x)_{2.03}\text{Cu}_{3.06}\text{O}_{10+x}$  ( $x=0.0\sim 0.06$ ).

Fig. 2 shows the fractional intensity of the 110 K phase for the same sample as was used for the data shown in Fig. 1. The peak intensities of the Miller indices (115) of the 110 K phase (at  $2\theta=26.2^\circ$ ) and the 80 K phase (at  $2\theta=27.5^\circ$ ) are employed here to estimate the volume fraction of the 110 K phase in the samples.

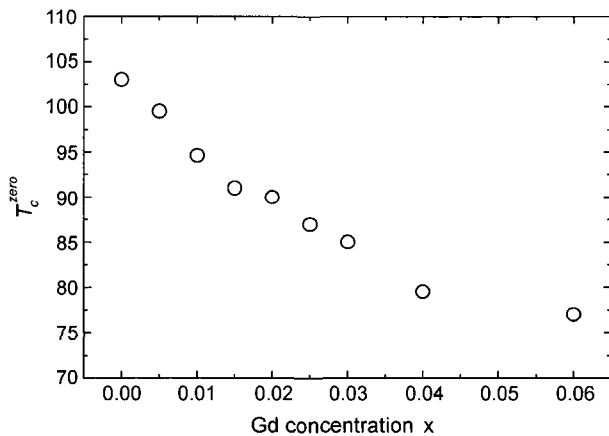
Fig. 3 shows the variation of the lattice constants  $a$ ,  $b$ , and  $c$  as a function of the concentration of  $x$  as it is substituted for Gd. These results were obtained from the X-ray powder diffraction patterns of the 110 K phase. As  $x$  increases, the  $c$ -, the  $a$ - and the  $b$ -axes gradually decreases in the range of  $x < 0.015$ . In the range of  $x \geq 0.015$ , the trend becomes ambiguous due to the presence of 80 K phase in the samples. Simi-



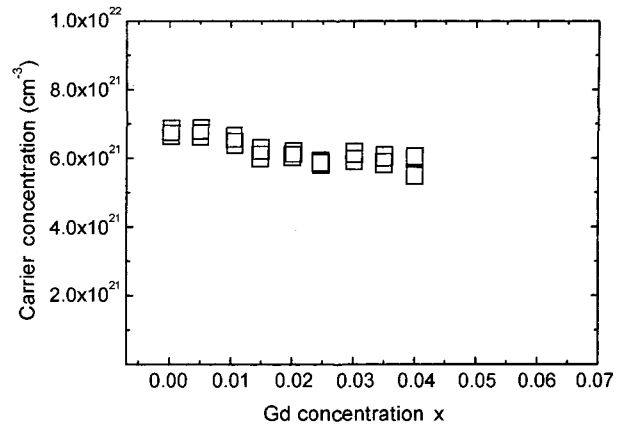
**Fig. 4.** Temperature dependence of the electrical resistivities for the samples with various Gd concentration in  $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{1.91}(\text{Ca}_{1-x}\text{Gd}_x)_{2.03}\text{Cu}_{3.06}\text{O}_{10+\delta}$  ( $x=0.0\sim 0.06$ ).

lar behaviour was observed in many experiments<sup>30-32</sup> involving substitution of other rare-earth elements. The decrease in the length of  $c$ -axis with increasing  $x$  is due to the smaller size of  $\text{Gd}^{3+}$  ions compared to the  $\text{Ca}^{2+}$  ions. However, it is very difficult to understand the decrease in the  $a$ - and  $b$ -axes as a result of substitution, since the length of both the  $a$ - and  $b$ -axes is controlled by the length of the in-plane Cu-O bond.

Fig. 4 shows the temperature dependence of the electrical resistivity for samples with various Gd concentrations. The critical temperature  $T_c$  gradually decreases with increasing  $x$ . Within the solubility limit of the 110 K phase, the sample contains only 110 K single phase. Therefore in the range of the 110 K single phase ( $x < 0.015$ ), the resistivity dependence shows a smooth curvature that is typical for the 110 K single phase (one step transition). However, in the range of  $x \geq 0.015$ , the resistivity curve shows an inflection due to the two step transition caused by an increase of the 80 K phase with increasing concentration  $x$ . In addition, for  $x=0.06$  composition, the resistivity dependence shows a smooth curvature that is typical of the 80 K single phase (one step transition), since the 110 K phase almost disappears with the increase in the 80 K phase.



**Fig. 5.** Variation of the carrier concentration with  $T_c^{\text{zero}}$  in the  $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{1.91}(\text{Ca}_{1-x}\text{Gd}_x)_{2.03}\text{Cu}_{3.06}\text{O}_{10+\delta}$  ( $x=0.0\sim 0.06$ ).



**Fig. 6.** Gd concentration dependence of the carrier concentration in  $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{1.91}(\text{Ca}_{1-x}\text{Gd}_x)_{2.03}\text{Cu}_{3.06}\text{O}_{10+\delta}$  ( $x=0.0\sim 0.06$ ).

Fig. 5 shows  $T_c^{\text{zero}}$  for the samples with various Gd concentrations. The resistivity curve of the undoped sample has a 110 K phase with an offset temperature ( $T_c^{\text{zero}}$ ) of 103 K. In the range of the 110 K single phase ( $x < 0.015$ ),  $T_c^{\text{zero}}$  straightly decreases in the ratio of 8.4 K/at% with increasing Gd concentration. The decrease in  $T_c^{\text{zero}}$  may be due to an decrease in the hole concentration in the Cu-O plane caused by substitution of  $\text{Gd}^{3+}$  for the  $\text{Ca}^{2+}$  site. In the range of  $x \geq 0.015$ ,  $T_c^{\text{zero}}$  for the samples reflect that of the 80 K phase mixed in the sample. Namely, in the range of  $x \geq 0.015$ , the ratio of decrease of  $T_c^{\text{zero}}$  comes to be small. And, for  $x=0.06$  composition,  $T_c^{\text{zero}}$  shows 76 K.

Fig. 6 shows the carrier concentration for samples with various Gd concentrations. The carrier concentration of the samples seems to decrease slightly with increasing Gd concentration  $x$ .

#### 4. Conclusions

We have prepared a number of  $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{1.91}(\text{Ca}_{1-x}\text{Gd}_x)_{2.03}\text{Cu}_{3.06}\text{O}_{10+\delta}$  ( $x=0.0\sim 0.06$ ) samples with different  $x$ . We obtained the 110 K single phase for samples with Gd concentrations  $x < 0.015$ . The 80 K phase appeared above  $x=0.015$ , and the 110 K phase almost disappeared above  $x=0.06$ . Within  $x=0.015$ , the  $c$ -axis in the samples of  $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{1.91}(\text{Ca}_{1-x}\text{Gd}_x)_{2.03}\text{Cu}_{3.06}\text{O}_{10+\delta}$  ( $x=0.0\sim 0.06$ ) decrease with increasing  $x$ , which is attributed to the smaller size of the dopant  $\text{Gd}^{3+}$  ions. The  $a$ - and  $b$ -axes on the other hand, decrease with  $x$  due to the decrease in the Cu-O bond length caused by the decrease in carrier concentration. The critical temperature,  $T_c$ , gradually decreased with increasing  $x$ . Until  $x=0.15$ , the decrease in  $T_c$  may be due to a decrease in hole concentration within the Cu-O plane of the 110 K phase. This decrease in hole concentration in the Cu-O plane is caused by the doping of trivalent ions ( $\text{Gd}^{3+}$ ) for the divalent Ca ion. Further decrease in  $T_c$  above  $x=0.015$ , the contribution from the 80 K phase could be considered.

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