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ORIGINAL PAPER

Boron Substitution for Bi in Sr-Free Bi-2212 Superconductor of $Bi_2Pr_{0.5}Ca_{2.5}Cu_2O_z$

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Abstract Boron substitution is tried for Bi in the Sr-free Bi-2212 compound of Bi–Pr–Ca–Cu–O, and the substitution effect on superconductivity of the compound is investigated. X-ray diffraction study shows that the samples are of almost the single phase in the x range of $0.0 \le x \le 0.4$ for the nominal composition of $(Bi_{2-x}B_x)Pr_{0.5}Ca_{2.5}Cu_2O_z$. Moreover, electrical resistivity and magnetic susceptibility measurements show that the superconducting transition temperature monotonously decreases with increase of x. From these results, it is first discovered that boron is a substitutable element for Bi in the Sr-free Bi-2212 compound and that the boron substitution causes the number of hole-carriers to decrease for this compound.

Keywords Boron substitution · Sr-free Bi-2212 phase · $Bi_2Pr_{0.5}Ca_{2.5}Cu_2O_z$ · Superconductivity

1 Introduction

Since three superconducting compounds with the ideal compositions of $Bi_2Sr_2CuO_z$ (2201 phase), $Bi_2Sr_2CaCu_2O_z$ (2212 phase), and $Bi_2Sr_2Ca_2Cu_3O_z$ (2223 phase) were discovered in the Bi–Sr–Ca–Cu–O system [1–3], new Bi superconductors have been eagerly searched on the basis of an idea of substituting by other elements for Sr or Ca in their structures. As a result, Sr-free Bi-superconductor containing the 2212 and 2201 phases, which showed superconductivity at about 52 K, was newly found in the Bi–La–Ca–Cu–O system [4]. Following this finding, we synthesized the extended family of the Sr-free Bi-2212 cuprates in the $Bi_2Ln_xCa_{3-x}Cu_2O_z$ (Ln = La, Pr, Nd, Sm, Eu, and Gd) system [5]. All samples were of almost the single 2212 phase for $x = 0.5$; among them, the sample with the nominal composition of $Bi_2Pr_{0.5}Ca_{2.5}Cu_2O_z$ showed resistivity-drop originating from superconductivity at about 70 K and zero resistivity at about 45 K. However, the superconducting transition temperature T_c is lower than that of the 2212 phase in Bi–Sr–Ca–Cu–O system. The T_c value of the 2212 phase is known to be about 80 K in Bi–Sr–Ca–Cu–O system; the value is reported to rise up to 98.5 K by substitution of Pb for Bi and annealing in N_2 or Ar [6]. Considering these results, we expect that the T_c value of the 2212 phase in the $Bi_2Ln_xCa_{3-x}Cu_2O_z$ system boosts up to the maximum value of the 2212 phase in the Bi–Sr–Ca–Cu–O system. We actually succeeded in making the T_c value higher, up to 80 K for the Sr-free Bi-2212 thin films of $Bi_2Ln_xCa_{3-x}Cu_2O_z$, which were synthesized by laser ablation method [7–9]. We desire to make the T_c value of the Sr-free Bi-2212 bulk sample even higher. So, we have attempted Pb-substitution and Cd-substitution for Bi in the Sr-free 2212 compounds. For the latter Cd-substitution, it was reported that the substitution could induce superconductivity in the non-superconducting Bi-2222 compound in spite of annealing under relatively low-pressure O_2 atmosphere [10]. Regrettably, it emerged that both substitutions of Pb and Cd were impossible for the $Bi_2Ln_xCa_{3-x}Cu_2O_z$ samples. Under these circumstances, we considered that discovery of new substitutable substances for Bi was the first step to boost up to the T_c values of the 2212 phase in the

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$Bi_2Ln_xCa_{3-x}Cu_2O_z$ system. Recently, we have discovered that boron was one of the new elements substitutable for Bi in the Bi-2212 compound of $Bi_2Sr_2CaCu_2O_z$ [11].

In this study, we have prepared samples partially substituted by boron for Bi in the Sr-free Bi-2212 compound of $Bi_2Pr_{0.5}Ca_{2.5}Cu_2O_z$ and we have investigated whether the substitution was possible, or impossible, and what is the effect of substitution on the superconductivity.

2 Experiment

Samples with a nominal composition of $(Bi_{2-x}B_x)Pr_{0.5}Ca_{2.5}Cu_2O_z$ were prepared for various x values by a conventional solid-state reaction method. Starting materials were Bi_2O_3, B_2O_3, Pr_7O_{11}, $CaCO_3$, and CuO powders with purities of 99.99%. These powders with the appropriate composition were mixed, thoroughly reground, and cold-pressed into disk-shaped pellets. The pellets were preheated at 780 °C for about 17 h in air and cooled down to room temperature. Then, the pellets were pulverized, pelletized, and sintered at 820 °C for about 17 h in O_2, and then cooled down to room temperature. Finally, the resulting pellets were pulverized, pelletized again, and sintered at 830 °C for about 17 h in O_2, and they were cooled down to room temperature at a rate of 0.5 °C /min.

X-ray powder diffraction measurements were carried out using CuKα radiation monochromatized with a curved graphite single crystal. The diffraction intensities were measured by step scanning at 0.02° intervals for 2 s in the range from 3° to 50° in 2θ. The temperature dependence of the electrical resistivity (hereafter, ρ–T dependence) was measured by a standard four-probe method using silver paste for the contacts. Moreover, the temperature dependence of the DC magnetic susceptibility (hereafter, χ–T dependence) was measured for the powdered samples using a SQUID magnetometer. The data were obtained on heating from 4.0 to 290 K within a magnetic field of 10 Oe after cooling from room temperature to 4.0 K under zero-magnetic field (ZFC condition).

3 Results and Discussion

X-ray diffraction analysis was carried out to investigate whether boron substitution for Bi in the $(Bi_{2-x}B_x)Pr_{0.5}Ca_{2.5}Cu_2O_z$ system was possible, or impossible, and if it was possible, what was the limit of solid-solution. Figure 1 shows X-ray diffraction patterns for the Bi-samples with $x = 0.0$, 0.2 and 0.4. The pattern of the sample with $x = 0.0$ can be seen as a standard because almost the single 2212 phase sample could be obtained for the composition of $Bi_2Pr_{0.5}Ca_{2.5}Cu_2O_z$ [5]. Obviously, the diffraction pattern is seen to be identical to that of the Bi-2212

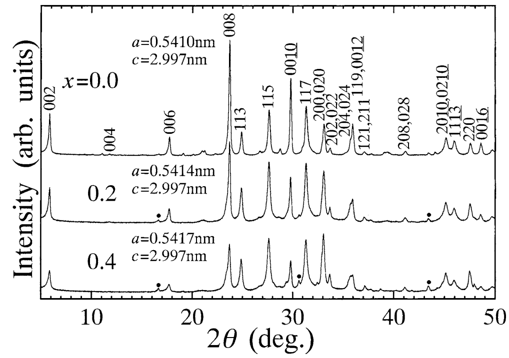

Fig. 1 Powder X-ray diffraction patterns for the samples with $x = 0.0$, 0.2 and 0.4 in the present $(Bi_{2-x}B_x)Pr_{0.5}Ca_{2.5}Cu_2O_z$ system. For an example, diffraction peaks of the sample with $x = 0.0$ are indexed on the basis of a pseudotetragonal unit cell with the lattice parameters $a = 0.5410$ nm and $c = 2.997$ nm

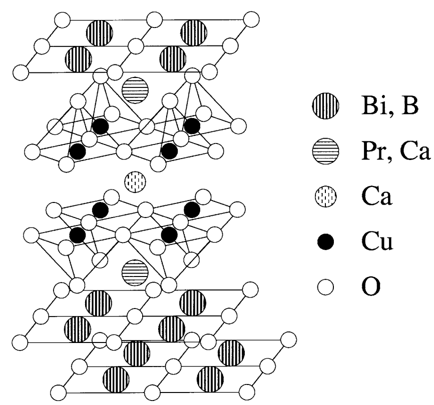

Fig. 2 A schematic representation of the crystal structure in the $(Bi_{2-x}B_x)Pr_{0.5}Ca_{2.5}Cu_2O_z$ system

phase and the diffraction peaks can be indexed on the basis of a pseudotetragonal unit cell with the lattice parameters $a = 0.5410$ nm and $c = 2.997$ nm. Then, if boron content x is increasing, diffraction pattern for each sample is the same as that of the standard sample, and almost the diffraction peaks can be attributable to those of the Bi-2212 compound. However, seeing every little thing for the diffraction pattern of the sample with $x = 0.4$, reflection peaks characterized by closed circles become higher as seen by comparison with the pattern of the sample with $x = 0.2$. The peaks come from impurity phases. Then, when content x comes to 0.6, the impurity phases dominated almost the sample although it is not shown in the figure. The impurities cannot be specified at present. The lattice parameters a and c are also given in the figure of each sample. We can see such a tendency that the value of a increases when x is increasing from 0.0, but that of c is constant. This tendency is similar to that in the $(Bi_{2-x}B_x)Sr_2CaCu_2O_z$ system [11]. From these results, it was found that boron was substitutable for Bi in the present $(Bi_{2-x}B_x)Pr_{0.5}Ca_{2.5}Cu_2O_z$

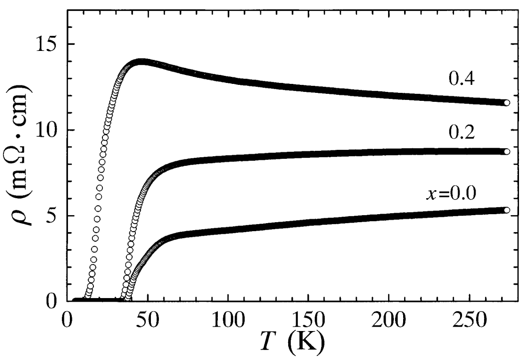

Fig. 3 ρ–T dependence for the samples with x from 0.0 to 0.4 in the $(Bi_{2-x}B_x)Pr_{0.5}Ca_{2.5}Cu_2O_z$ system

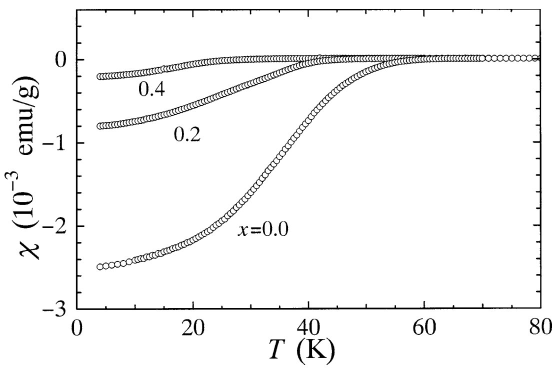

Fig. 4 χ–T dependence on the ZFC condition for powdered samples with x from 0.0 to 0.4 in the $(Bi_{2-x}B_x)Pr_{0.5}Ca_{2.5}Cu_2O_z$ system. The applied field is 10 Oe

system and the substitution limit's vicinity was close to $x = 0.4$. A schematic representation of the crystal structure for the present $(Bi_{2-x}B_x)Pr_{0.5}Ca_{2.5}Cu_2O_z$ system is shown in Fig. 2.

Figure 3 shows ρ–T dependence for the samples with x from 0.0 to 0.4 in the $(Bi_{2-x}B_x)Pr_{0.5}Ca_{2.5}Cu_2O_z$ system. We can see that the sample with $x = 0.0$ shows metallic-like ρ–T dependence and it has the smallest $\rho_{273\ K}$ which is the value of resistivity at 273 K. Then, this $\rho_{273\ K}$ for each sample is seen to be increasing with increase of x from 0.0. Moreover, we can see that each sample shows a resistivity-drop in the temperature range from 30 to 70 K. The resistivity-drop originates from superconducting transition of the Bi-2212 phase. The onset temperature of the resistivity-drop is found to be gradually falling down with increase of x. As is well known for the high-T_c cuprate superconductors, the T_c value correlates with the hole-concentration p per Cu atom, and the value shows the so-called bell-shaped behavior as a function of p [12–14]. From this fact and the results of the resistivity measurements described above, it can be considered that the boron substitution causes the hole-concentration to decrease and this decrease makes the superconducting temperature T_c lower in the present $(Bi_{2-x}B_x)Pr_{0.5}Ca_{2.5}Cu_2O_z$ system, as the samples are considered to be in the underdoped region where the hole-concentration is not adequate to that claimed necessary for causing the sample to show the optimal T_c.

Figure 4 shows χ–T dependence for powdered samples with x from 0.0 to 0.4 in the present $(Bi_{2-x}B_x)Pr_{0.5}Ca_{2.5}Cu_2O_z$ system. Each sample is seen to show a diamagnetic signal originating from superconductivity of the Bi-2212 phase. The onset temperature of the signal, namely T_c, is gradually falling down with the increase of boron content x from 0.0 to 0.4. This result is consistent with that of the ρ–T dependence shown in Fig. 3. It is certain that the present Sr-free Bi-2212 phase is in the underdoped state, the hole-concentration decreases by increasing the content of boron substituted for Bi, and then, while the superconducting volume becomes small, the superconducting temperature T_c becomes lower.

We have already reported synthesis of the Sr-free Bi-2201 cuprates of $Bi_2Ln_xCa_{2-x}CuO_z$ [15, 16]. It is worth mentioning that boron is also substitutable for Bi of the cuprates. Continuative studies on such a new trial as double-substitution of boron for Bi and Na for Ca hereafter are needed to obtain the Sr-free Bi-2212 samples showing higher T_c.

4 Concluding Remarks

We investigated possibility of boron-substitution for Bi and the substitution effect on superconductivity of the Sr-free Bi-2212 compound of $Bi_2Pr_{0.5}Ca_{2.5}Cu_2O_z$. From X-ray diffraction study, it was clear that boron was substitutable for Bi, and the substitution limit's vicinity was close to $x = 0.4$ in the $(Bi_{2-x}B_x)Pr_{0.5}Ca_{2.5}Cu_2O_z$ system. From the electrical resistivity and magnetic susceptibility measurements, we also obtained the experimental result that T_c was decreasing with the increase of x from 0.0 to 0.4. The latter result is considered to show that the substitution of boron for Bi causes the number of hole-carriers to decrease in the present $(Bi_{2-x}B_x)Pr_{0.5}Ca_{2.5}Cu_2O_z$ system.

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