

## Superconducting PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub>

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PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> grown by the traveling-solvent floating-zone method shows a large inhomogeneity both in structural and physical properties, such as lattice parameters and transport and magnetic properties. Some parts of this sample exhibit bulk superconductivity. The *c*-axis lattice constant is longer than that of nonsuperconducting samples grown by the flux method. However, the magnetic susceptibility of the superconducting sample suggests the valence of Pr is +3. The superconducting transition temperature exceeds 100 K under a pressure over 8 GPa and still has a potential to increase. [S0031-9007(97)05151-X]

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It has been believed that in the RBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> (*R*123) series the *R* = Pr system is an insulator and the strong hybridization of Pr 4*f* and O 2*p* orbitals leads to localization of oxygen holes [1–3]. Extensive studies have been performed to make SIS (superconductor/insulator/superconductor) junctions using insulating Pr123, since it has the same structure with the superconducting Y123. However, in some cases they claimed that the Pr123 is not a good insulator but a metal [4,5]. The condition to make a good insulating Pr123 is not so clear. On the other hand, Blackstead *et al.* [6] reported that a thin film of Pr123 exhibits diamagnetism which seems to be due to superconductivity with the volume of at most 7%.

Recently, we have observed bulk superconductivity in the sample prepared by the traveling-solvent floating-zone (TSFZ) method [7,8]. These results showed that the physical properties of the Pr123 system change with the growth condition from insulator to metal or superconductor. We have studied the structure of TSFZ grown crystal and compared details of the structures with that of crystals grown by the conventional flux method [9–11] and found a clear difference between the two structures [12]. The superconducting critical temperature *T<sub>c</sub>* of oxygen annealed crystals distributes from zero to ~80 K. Conditions which produce superconductivity in Pr123 are important to make clear the mechanism of high *T<sub>c</sub>*. Furthermore, we need to know details of growth conditions of insulating and superconducting Pr123 for making good SIS junctions in applications to electronics. In the present paper, we report the characteristics of the superconducting Pr123, such as crystal structure and magnetic properties, as well as high pressure effects.

In sample preparation predried Pr<sub>6</sub>O<sub>11</sub>, BaCO<sub>3</sub>, and CuO with the purity of 99.99% were used as starting materials. In the TSFZ method, single crystals were grown using an infrared radiation furnace with four 300 kW halogen lamps as radiation sources in flowing argon gas with 0.1% oxygen. The details of crystal growth will be published elsewhere [13,14]. The as-

grown crystals were annealed in an α-Al<sub>2</sub>O<sub>3</sub> crucible at 850 °C for 24 hours and then at 550 °C for 77 hours in flowing pure oxygen gas. There is no chemical reaction between crystals and the crucibles to be observed by x-ray energy-dispersive spectrometry (EDS) analysis.

It is well known that flux grown crystals are insulators, but the TSFZ grown crystals showed a wide variety of conducting properties from insulator to metal. The as-grown TSFZ crystals were spontaneously broken into small pieces with a size of ~1 mm<sup>3</sup>, when they were kept in air for over one week. After the annealing of the pieces some exhibit superconductivity with the *T<sub>c</sub>* ranging from ~25 to ~80 K determined from the zero-resistivity transition [14]. Figure 1 shows the resistivity of several annealed pieces. In the magnetization measurement, the sample with *T<sub>c</sub>* ~ 80 K shows a complete diamagnetism and the Meissner effect of ~15% [7]. We examined the atomic ratio and the crystal structure of these superconducting pieces.

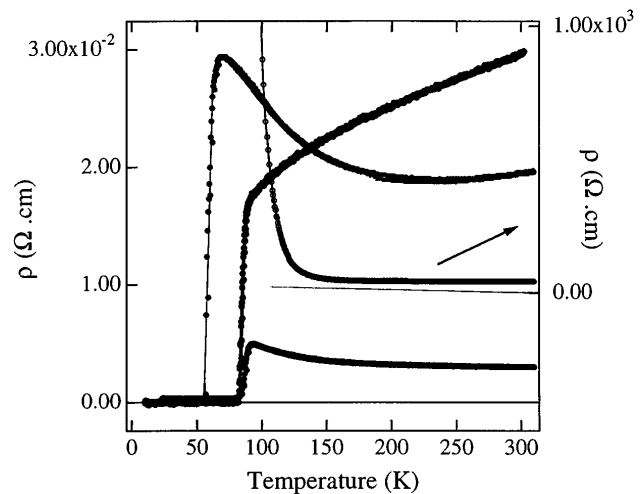


FIG. 1. Resistivity of several Pr123 crystal pieces grown by the TSFZ method.

The crystal structure was investigated using an x-ray precession camera with imaging plate and a Rigaku-AFC-7R four-circle x-ray diffractometer with monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). The as-grown pieces of TSFZ crystal are tetragonal with space group  $P4/mmm$ , and annealed pieces of TSFZ crystal are orthorhombic with space group  $Pmmm$ . However, the lattice parameters of superconducting crystals are slightly different from piece to piece. For example, the value of  $c$ -axis lattice constant scatters from 11.71 to 11.83  $\text{\AA}$ . The average lattice parameters of typical pieces with  $T_c \sim 80 \text{ K}$  are  $a = 3.872(4)$ ,  $b = 3.931(1)$ , and  $c = 11.77(2) \text{ \AA}$ . The chemical composition of these pieces was examined by the inductively coupled plasma atomic emission spectrometer and SEM-EDS methods. The average ratio of Pr:Ba:Cu was 1.05:1.95:2.96. From these experimental results we confirmed that the superconducting pieces have the Y123 structure. However, the  $c$ -axis lattice constant is longer than the one previously reported for flux grown crystals [9].

The direct structural analysis of superconducting and nonsuperconducting crystals is the most perfect research to know the difference between both crystals. Unfortunately, since the superconducting sample has twin structure and the structurally completely uniform region in the sample piece is less than submillimeter scale, we have studied the detailed structural difference between TSFZ and flux grown crystals using as-grown samples. It has been known that the structural difference between annealed and as-grown crystals is to be caused by oxygen change for Y123 systems. However, since the flux grown crystals show no superconductivity even after the oxygen annealing, we believe that there must be some difference even in as-grown states between the flux and TSFZ grown crystals. Therefore, it is meaningful to study the structural difference in both as-grown crystals to investigate the origin of superconductivity in Pr123 grown by the TSFZ method. A modified structure was observed in both crystals.

The  $c$ -axis lattice constant of as-grown TSFZ crystals scatters from 11.879(4) to 11.836(2)  $\text{\AA}$  refined by the least-squares method using 25 reflections with  $2\theta > 65^\circ$ . The  $c$ -axis lattice constant is much longer than observed values in as-grown samples of other R123 systems. A single crystal with lattice parameters of  $a = 3.909(5)$  and  $c = 11.836(2) \text{ \AA}$  was used for the structural analysis. The results of refinements of the average structure using 5961 reflections yielded the unweighted and weighted  $R$  factors,  $R = 2.5\%$ ,  $wR = 3.0\%$  in space group  $P4/mmm$ . The atomic coordinates and equivalent thermal parameters of as-grown TSFZ crystal are listed in Table I. The schematic structural diagram of the tetragonal Pr123 is shown in Fig. 2. The  $z$  positional parameter of the Ba site in Table I is larger than that of flux grown crystals [9,10], but the distance between the Cu(1)-O(1) chain to the Cu(2)-O(2) plane seems to have little difference between the TSFZ crystal [4.1655(5)  $\text{\AA}$ ],

TABLE I. Structural parameters for as-grown TSFZ Pr123 crystal.

Atom	$x$	$y$	$z$	$^b B_{\text{eq}}$
Pr	0.5000	0.5000	0.5000	0.480(2)
Ba	0.5000	0.5000	0.19052(2)	0.815(2)
Cu(1)	0.0000	0.0000	0.0000	1.097(5)
Cu(2)	0.0000	0.0000	0.35193(4)	0.539(3)
O(1) <sup>a</sup>	0.0000	0.5000	0.0000	2.0000
O(2)	0.5000	0.0000	0.3706(2)	0.69(2)
O(4)	0.0000	0.0000	0.1526(3)	1.69(3)

<sup>a</sup>Occupancy of the O(1) site was refined to be about 8%;  $B_{\text{eq}}$  was set to be 2.

<sup>b</sup> $B_{\text{eq}} = \frac{8}{3} \pi^2 [U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12} aa^* bb^* \cos \gamma + 2U_{13} aa^* cc^* \cos \beta + 2U_{23} bb^* cc^* \cos \alpha]$ .

and the flux crystal ( $\sim 4.1701$ – $4.1633 \text{ \AA}$ ) [10]. However, the distance between the two Cu(2)-O(2) planes expands slightly from the flux crystal ( $\sim 3.4838$ – $3.4875 \text{ \AA}$ ) [10] to the TSFZ crystal [3.5053(9)  $\text{\AA}$ ]. The expansion of the Cu(2)-Cu(2) distance seems leading to the longer  $c$  axis in TSFZ crystals.

The inverse magnetic susceptibility of superconducting Pr123 is shown in Fig. 3 up to 300 K in an applied field of 0.5 T. From the fit to the Curie-Weiss law [ $\chi = \chi_0 + C/(T + \Theta)$ ], we obtained  $\chi_0 = 4.5 \times 10^{-4} \text{ emu/mol}$  and effective magnetic moment of  $\mu_{\text{eff}} = 2.92 \mu_B$ . Although the free ion of  $\text{Pr}^{3+}$  is  $3.58 \mu_B$  [15], accounting for the crystal-field effect in Pr123, many authors have reported that the value is about  $2.87 \mu_B$  [16]. The effective magnetic moment of TSFZ crystal is in good agreement with that of flux crystals. This suggests that Pr in both TSFZ and flux crystals might have the same  $\text{Pr}^{3+}$  state.

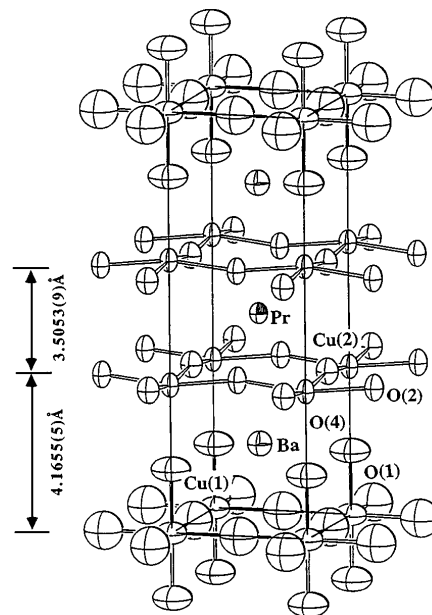


FIG. 2. Schematic structure of the tetragonal phase of Pr123 grown by the TSFZ method.

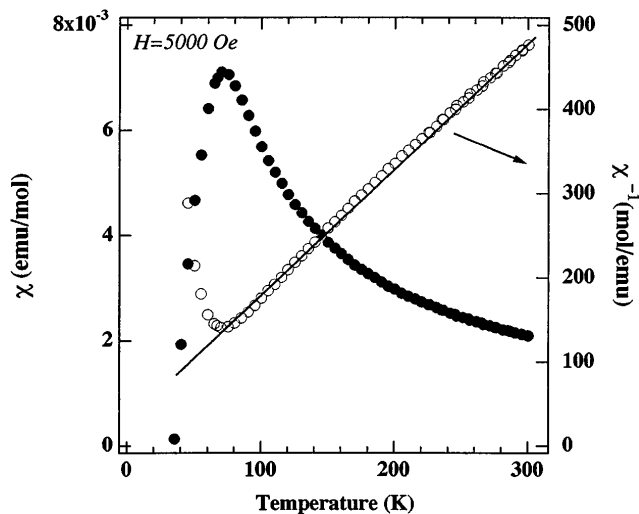


FIG. 3. Temperature dependence of inverse susceptibility of the superconducting Pr123. The solid lines represent fits of the data to the Curie-Weiss law.

On the other hand, the susceptibility at low temperatures is different between the two samples. The flux grown sample shows a clear kink at  $T_N = 17$  K [17]. However, as-grown TSFZ crystal shows only a small broad peak anomaly around 16 K [18]. The results suggest the TSFZ crystal has a large inhomogeneity not only in transport properties but also in magnetic properties. In the superconducting crystal we cannot observe a trace of antiferromagnetism of Pr down to 4 K.

The temperature dependence of the electrical resistivity under high pressure was investigated with the dc four-probe method using a cubic anvil apparatus. Figure 4 shows the pressure effect of  $T_c$  for the sample with  $T_c \sim 85$  K. The  $T_c$  was determined from the onset of transition in resistance temperature curves. The width of transition is about 3.5 K. A remarkable increase in  $T_c$  is observed, as those reported for many underdoped superconducting oxides. The  $dT_c/dP$ , where  $P$  is pressure, is known to be considerably small for the  $R\text{Ba}_2\text{Cu}_3\text{O}_x$  compounds whose oxygen content  $x$  is close to 7.0. Thus, it is worth indicating that the pressure dependence of  $T_c$  for Pr123 with  $T_c = 85$  K is much larger ( $dT_c/dP$  is about 3.5 K/GPa) than that for the optimally doped isostructural Y123 superconductor, where the  $dT_c/dP$  is about 0.4 K/GPa. The pressure effect shows an opposite behavior also for Pr doped Y123 compounds. This may lead to the conclusion that the Pr doped Y123 has a different electronic structure with the present superconducting compound. However, it is not easy to figure out the origin of that at present. The details of the pressure effect will be published elsewhere [19].

To remove the localization of holes due to strong hybridization between Pr  $4f$  and O  $2p$  orbitals, we can think about two possible ways. One is elongation of atomic distance between Pr and O(2). The other is substitution of Ba for Pr. It is well known in the

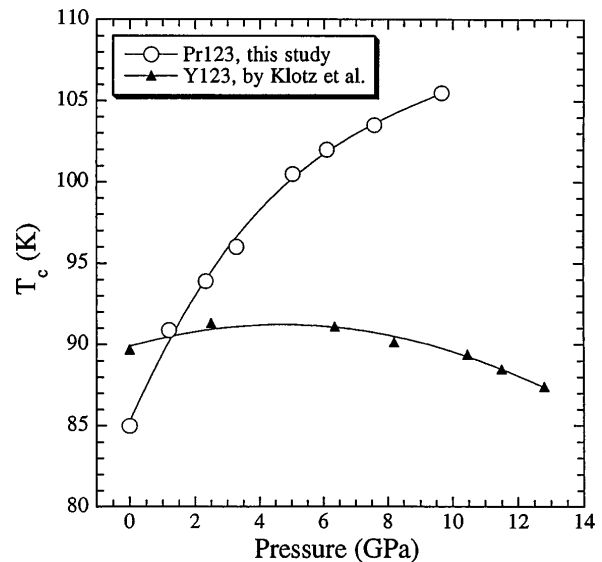


FIG. 4.  $T_c$  of Pr123 as a function of pressure. The data of Y123 are those from Ref. [18].

light rare-earth systems the substitution between Ba and rare earth easily occurs. In the R123 system this effect degrades superconducting properties [20,21].

In the superconducting Pr123 the  $c$ -axis lattice constant is longer than that of the flux samples. Figure 5 shows the relation between  $c$ -axis lattice constant and  $R^{3+}$  ionic radius of the superconducting R123 series [9]. The value of superconducting Pr123 falls in the consistent curve of other superconducting R123 systems. However, the value of nonsuperconducting crystal grown by the flux method reveals a departure from the curve as shown in Fig. 5 [10]. As shown in the previous section, the elongation of the  $c$ -axis lattice constant of TSFZ crystals is attributed to the elongation between Cu(2)-O(2) and Cu(2)-O(2) planes. The Pr and O(2) distance has a little difference between the flux crystal [2.479(2) Å] [10] and the TSFZ crystal [2.481(1) Å]. Although the expansion of the Cu(2)-Cu(2) distance seems to support that the elongation of the  $c$ -axis lattice constant may be an origin of hole delocalization, the Pr and O(2) distance has only a small difference. It is hard to consider at present experimental accuracy that the elongation of Pr and O(2) distance led to hole delocalization and produce superconducting in TSFZ Pr123 crystal. In addition, if we assume that the application of pressure decreases the Pr-O(2) distance, the experimental results in Fig. 5 contradict the idea that with increasing hybridization the localization of carriers becomes strong. Judging from the strong sample inhomogeneity the substitution of Ba for Pr might also contribute to the hole delocalization, but further structural analysis is necessary. Relatively high resistivity of the superconducting sample in Fig. 1 may result from this randomness.

The  $T_c$  of R123 systems has a close relation with hole concentration and the upper limit  $T_c$  is  $\sim 90$  K. In Fig. 4

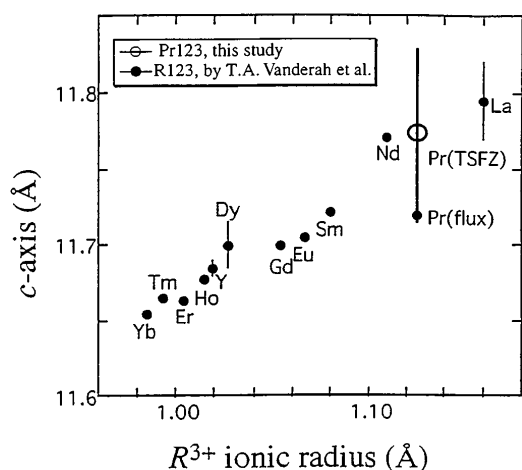


FIG. 5.  $R^{3+}$  ionic radius dependence of the  $c$  axis in  $R123$  systems. The data, except for Pr, are those from Ref. [9].

comparison of the pressure effect of  $T_c$  between Pr123 and Y123 is shown. In Y123 with the optimum oxygen concentration the  $T_c$  changes little with pressure around 92 K up to  $\sim 3$  GPa and decreases with pressure above 4 GPa [22]. However, the  $T_c$  of Pr123 increases from 85 to over 100 K rapidly with pressure and still increases up to 10 GPa. The result shows that the limit of  $T_c$  in Pr123 is different from those of other  $R123$  systems. It is known in many oxide superconductors that the increase in  $T_c$  at high pressure is due to the increase of superconducting carrier density [23]. Therefore, the present result requests us to reconsider the position of carriers in Pr123 system. This will give us useful information on the mechanism of high  $T_c$ .

In summary, the physical properties of the Pr123 system change with the growth condition. The sample grown from the melted state has a large inhomogeneity both in structural and physical properties, such as lattice parameters and transport and magnetic properties. In these samples some parts exhibit bulk superconductivity. Though a structural anomaly like the shortness of the  $c$  axis is pointed out in the nonsuperconducting sample grown by the flux method, this superconducting part has an ideal Y123 structure in the series of  $R123$  systems. However, the superconducting transition temperature exceeds 100 K under pressure. The fact that the transition temperature reaches higher than  $\sim 90$  K suggests the superconducting state of Pr123 will be different from other  $R123$  systems. The study of superconductivity in the Pr123 system will provide useful information on the physics of the high- $T_c$  mechanism and also on making stable insulating films for application to electronics.

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