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Growth and anisotropic resistivity of $PrBa_2Cu_4O_8$ and $Pr_2Ba_4Cu_7O_{15-y}$ single crystals: A direct probe of metallic Cu-O double chains

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We have successfully grown single crystals of $PrBa_2Cu_4O_8$ (Pr124) and $Pr_2Ba_4Cu_7O_{15-y}$ (Pr247) by means of a flux method under high pressure oxygen gas of 11 atm in Al_2O_3 or MgO crucibles. The most appropriate starting composition for the crystal growth was found to be Pr:Ba:Cu=1:2:3 for both Pr124 and Pr247, by examining the generated phases in samples prepared with widely varying composition and sintering temperature. The temperature dependence of resistivity of Pr124 single crystals exhibited no superconductivity, at least down to 2 K. Resistivity along the *b*-axis direction showed a highly conductive behavior, of which the origin is attributed to the double-chain site because of the large anisotropy between *a*- and *b*-axis resistivities. The anisotropy in resistivity between the *a*- and *b*-axis directions was found to be about 17 at room temperature, 275 at 85 K, and 190 at 5 K.

I. INTRODUCTION

The discovery of high-temperature superconductors has stimulated many studies of strongly correlated systems in low-dimensional materials. While two-dimensional (2D) systems have a direct relevance to high-temperature superconductivity, experimental studies on one-dimensional (1D) systems are of importance as well because of the existence of exact solvable theoretical models. Particularly interesting is the metallic state in a 1D system, the Tomonaga-Luttinger liquid state, which is believed to be essentially different from the Fermi liquid state.

In this context, the Cu-O chain structure found in some cuprates is attracting interest, since they might exhibit 1D metallic character if a proper amount of carriers were doped. There are two kinds of structurally different Cu-O chains in cuprates: an edge-sharing chain in which the edges of adjacent CuO_4 squares are shared, and a corner-sharing chain consisting of corner linked squares. Accordingly, the bonding angle of Cu-O-Cu of the former type of CuO chains is 90°, while that of the latter is 180°.

Hayashi *et al.* studied magnetic and transport properties of polycrystalline $(Ca,Y)_4Cu_5O_{10}$, which possesses the former type of chain, and claimed the formation of Zhang-Rice singlets in this system.[1] On the other hand, Kim *et al.* studied $SrCuO_2$, one of the corner-sharing CuO chain materials, by means of an angle-resolved photoemission spectroscopy (ARPES).[2] The result was interpreted as a strong indication of spin-charge separation, an interesting claim in the relation with the nature of 1D systems. However, to the best of our knowledge, no one has succeeded in doping $SrCuO_2$ so far, and studying the metallic state of a 1D system using this compound is still not possible.

The three phases of the Y-Ba-Cu-O system also possess corner-sharing Cu-O chain structure. These phases, $YBa_2Cu_3O_{7-y}$ (Y123), $YBa_2Cu_4O_8$ (Y124), and $Y_2Ba_4Cu_7O_{15-y}$ (Y247), are characterized by the layered perovskite structure with the possession of Cu-O chains and superconducting 2D CuO_2 planes. The structural difference originates from the different stacking sequence of the Cu-O chain: the repetition of a single-chain, that of the double-chain and the alternative repetition of a single- and double-chain for Y123, Y124, and Y247, respectively. Resistivity along the Cu-O chains are reported to be metallic with a temperature squared dependence from the comparison between the resistivities along the *a* and *b* axes both for Y123 (Ref. 3) and Y124 (Ref. 4) single crystals. Hence, these chains can be thought of as possible candidates for studying 1D metallic conductors. However, transport measurements can probe the chain sites only indirectly in the Y-Ba-Cu-O system, because of the presence of the highly metallic CuO_2 plane.

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It is well known that substitution of Pr for Y in Y123 drastically suppresses superconductivity, and changes the material to an insulator.[5] Similar to $SrCuO_2$, ARPES study has recently confirmed the presence of separated dispersions due to holons and spinons in the Cu-O chain site of $PrBa_2Cu_3O_{7-y}$ (Pr123).[6] Further, unlike $SrCuO_2$,[7] the Cu-O chain in Pr123 was suggested to possess a metallic character[8] from optical studies. However, the transport measurements revealed nonmetallic behavior along the *b*-axis direction of Pr123.[9] In contrast to Pr123, on the other hand, resistivities measured on polycrystalline $PrBa_2Cu_4O_8$ (Pr124) and $Pr_2Ba_4Cu_7O_{15-y}$ (Pr247) samples behaved metallic with a positive temperature coefficient of resistivity (TCR) below 180 K (Refs. 10–13) and 150 K,[12,13] respectively, although no superconductivity was detected. The results of a high-pressure study of these phases suggested that the metallic conduction is governed by the double Cu-O chains, while the semiconducting behavior at higher temperature by the CuO_2 plane.[12]

The metallic behavior along the Cu-O chain in Pr124 deserves attention because it may provide an unique and interesting opportunity for testing theories of 1D conductors. Terasaki *et al.*[14] measured magnetoresistance and Hall coefficient on a *c*-axis aligned Pr124 polycrystalline sample. They have interpreted their results as an indication of a dimensional crossover at about 100 K, below which the system becomes 2D due to interchain conduction along the *a*-axis direction. However, a direct study of the anisotropy between the *a*- and *b*-axes conduction has not been possible so far, because of the lack of single crystals.

Here, we report on the successful preparation of Pr124 and Pr247 single crystals. We first determined the appropriate conditions for single crystal growth by processing samples with various starting composition and heat-treatment temperatures. Using those results, we have successfully grown single crystals of Pr124 and Pr247, characterized them by x-ray diffraction methods, and studied the resistivity anisotropy of Pr124.

II. EXPERIMENT

In order to determine the ratio of Pr:Ba:Cu appropriate for the starting composition, we examined the sintering temperature dependence of the produced phases in samples, which had fifteen different compositions and were heat-treated under pure oxygen gas with a pressure of 11 atm. The presintered samples were prepared by mixing appropriate amounts of Pr_6O_{11}, BaO_2, and CuO, and subsequently calcinating the mixture at 800 °C for 20 h and at 830 °C for 20 h in air with intermediate regrounding. These powders were then pressed into pellets and sintered for 20 h at a temperature that was varied for each sample in the range of 975–1000 °C with an interval of about 5 °C under $P(O_2) = 11$ atm.

As will be described in detail below, the ratio of Pr:Ba:Cu of the starting composition most appropriate for the crystal growth was determined to be 1:2:3. Therefore, the single crystals were grown from presintered Pr123 powders by means of a high-oxygen pressure flux method with $P(O_2) = 11$ atm in Al_2O_3 or MgO crucibles. The heat-treatment profile is as follows; presintered powders of 50 g in weight was heated up to 1040 °C and held there for 12 h. After rapid cooling down to an appropriate temperature (T_s) in 0.5 h, the sample was slowly cooled to 970 °C with a rate of less than 1 °C/h followed with a furnace cooling to room temperature. The reactant was crashed and checked by powder x-ray diffraction method using CuKα radiation to determine the generated phases. The x-ray diffractometer was also used for identifying the phase of the single crystals, while the detailed crystal structure was examined by a precession camera with MoKα. The composition of one of the single crystals was quantitatively determined by inductively coupled plasma atomic emission spectrometry analysis. This crystal was used as a standard reference for the determination of compositions of other crystals by scanning electron microscope energy dispersed x-ray micro analysis (SEM-EDX). Electrical resistivity was measured with the DC four-probe method for *a* and *b* axes in the temperature range 2–300 K.

III. RESULTS AND DISCUSSION

A. Determination of the starting composition

The Pr124 and Pr247 phases are usually stable at lower temperatures than the Pr123 phase. We have previously studied the phase diagrams of Pr124 and Pr247 compositions by changing the sintering temperature and the oxygen pressure up to 9 atm. According to that result, the oxygen pressure at which the Pr124 phase is adjacent to the liquid phase can be estimated to be about 15–20 atm. Therefore, at $P(O_2) = 11$ atm, which is the maximum pressure allowed for our furnace, a simple slow-cooling process from the liquid phase should result into the growth of Pr123 single crystals. If, however, the melt is quenched fast enough to a temperature where the Pr124 phase is stable, skipping the Pr123 region, single crystals of Pr124 might grow. To apply this idea, it is necessary to determine the composition where the width between the liquid and Pr124 phases is narrow enough along the temperature axis.

We selected five compositions along each line connecting $PrBa_2O_x$ with CuO (line *A*), $PrBaO_3$ with $Ba_2Cu_7O_x$ (line *B*), and Pr_2BaO_x with $Ba_3Cu_7O_x$ (line *C*) on the PrO_x-BaO-CuO ternary phase diagram as shown in Fig. 1.

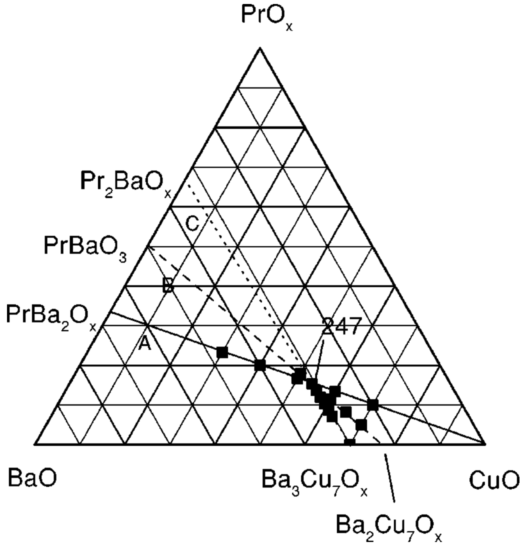

FIG. 1. PrO_x-BaO-CuO ternary diagram indicating the fifteen compositions selected for the determination of the appropriate starting composition for the crystal growth by solid squares.

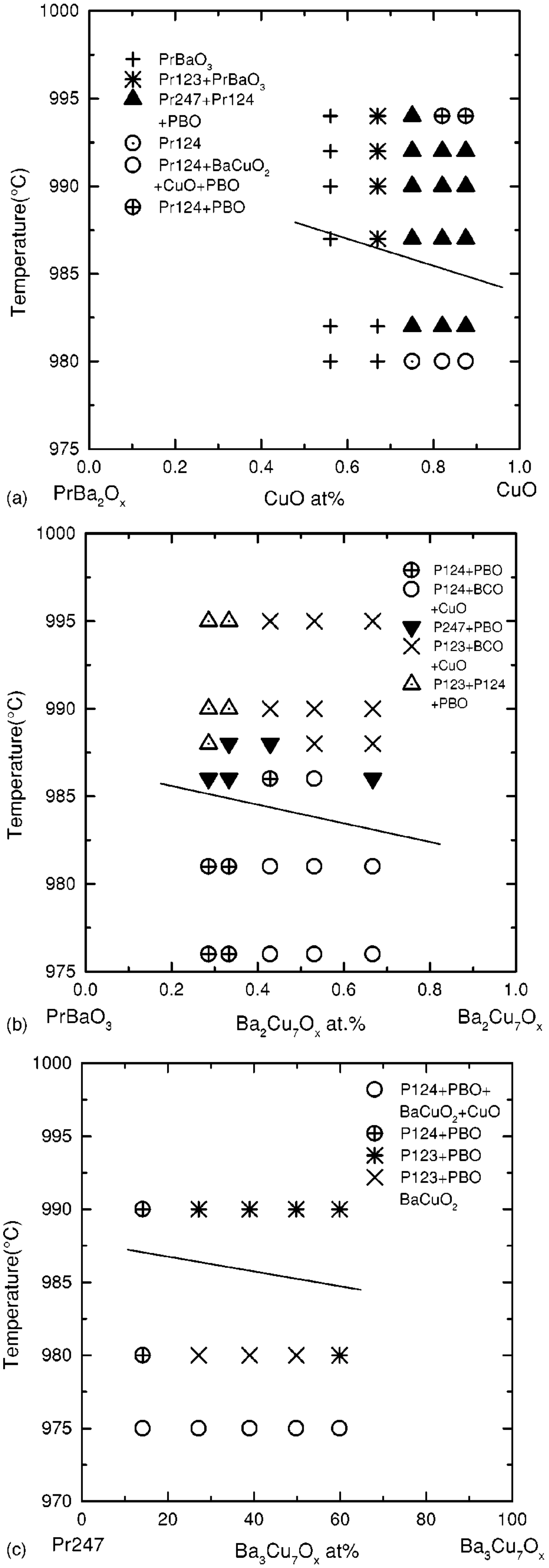

FIG. 2. The processing temperature and composition dependence of the generated phases in samples heat-treated under $P(O_2)=11$ atm. The composition was changed along line *A* (a), line *B* (b), and line *C* (c) of Fig. 1.

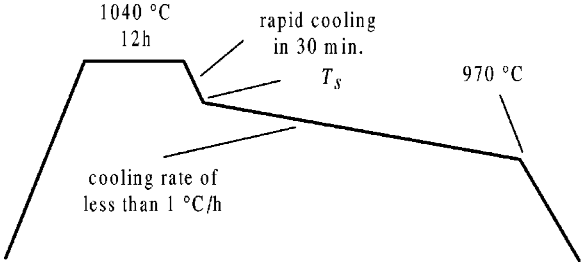

FIG. 3. The heat treatment profile for the growth of Pr124 and Pr247 single crystals.

These samples were sintered at various temperatures in the range of 975–1000 °C under $P(O_2)=11$ atm, and were characterized by the powder x-ray diffractometer method. The relations of the resultant phases to the sintering temperature and composition are shown in Figs. 2(a)–(c). The solid lines in these figures indicate the melting temperature, which was roughly estimated from the change in the shape of the pellet and the amount of melt flowed out during heat-treatment. Along line *A*, the ratio of $PrBa_2O_x$ to CuO is changed, and hence, Pr:Ba is fixed to 1:2. As shown in Fig. 2(a), none of the Pr-Ba-Cu-O phases are detected at all when CuO is poor. With increasing the content of CuO, Pr123 starts to grow, followed by the appearance of Pr124 and Pr247 phases. The Pr124 phase becomes stable even at high temperature in the CuO-rich region, indicating that CuO promotes the synthesis of Pr124. On the other hand, the results along lines *B* and *C* [Figs. 2(b) and (c)] show that the simultaneous increase of Ba and Cu unfavors the growth of Pr124 and Pr247 phases. Therefore, CuO rich starting composition is suitable for our purpose. However, if the starting composition contains too much CuO the amount of crystals would decrease because of the relative decrease in the amount of Pr. Altogether, we concluded that the most appropriate starting composition for the single crystal growth of Pr124 and Pr247 is Pr:Ba:Cu=1:2:3.

B. Growth and characterization of Pr124 and Pr247 single crystals

Single crystals were first grown in Al_2O_3 crucibles using the heat profile shown in Fig. 3 with various T_s (T_s =1040, 1025, 1020, 1005, and 1000 °C). X-ray diffraction patterns of the resultants are shown in Fig. 4. $T_s=1040$ °C means that no rapid cooling process was involved in the heat treatment, and, as evident from Fig. 4, the Pr-Ba-Cu-O phase thus obtained was the 123 phase. The intensity of the diffraction peaks due to $PrBaO_3$ phase increased with the width of the rapid cooling step (decreasing T_s). This is probably because $PrBaO_3$ is stable at 1040 °C, and the increase in the cooling step quenches this high-temperature phase. Further, with increasing the width of rapid cooling, diffraction peaks due to Pr247 and Pr124 phases appeared, indicating that the rapid cooling process is indeed effective for the formation of these phases. In fact, we could pick up Pr247 single crystals from the reactants processed with $T_s=1020$ and 1005 °C, and *c*-axis oriented mosaic Pr124 samples from that with $T_s=1000$ °C.

We have also carried out the same heat treatment using MgO crucibles. In this case, Pr124 single crystals were ob-

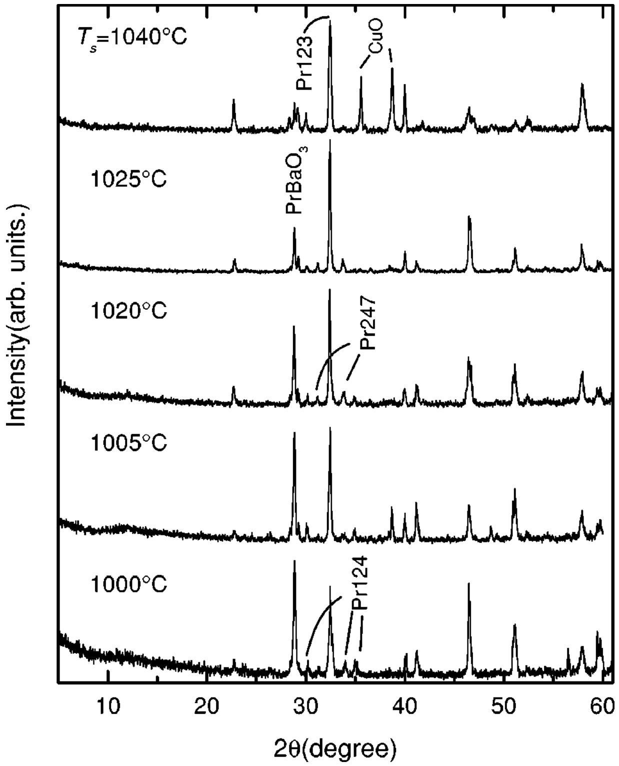

FIG. 4. Powder x-ray diffraction patterns of samples grown by the heat treatment shown in Fig. 3 with various T_s.

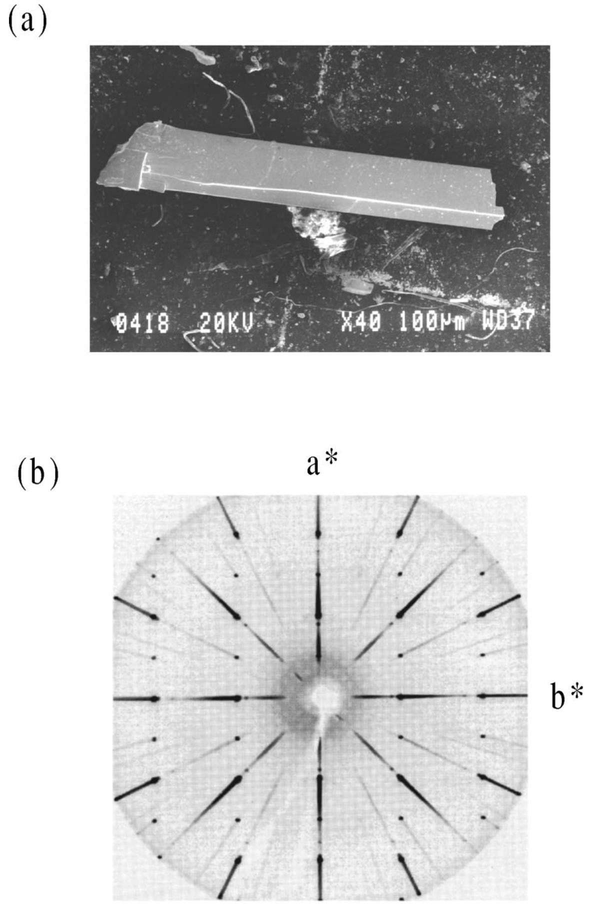

FIG. 5. A SEM image (a) and a $(hk0)$ precession pattern (b) of one of the Pr124 single crystals.

tained with $T_s = 1020\,°\mathrm{C}$, although Pr247 single crystals were grown with the same value of T_s in Al_2O_3 crucibles. The difference in the grown phase with the same T_s for these two crucibles is probably because Al has a much higher solubility into the liquid phase than Mg and/or because these two impurities substitute different Cu sites. Erb *et al.*[15] reported that the melt of Pr-Ba-Cu-O in Al_2O_3 crucibles is contaminated with 5 wt% of Al. On the other hand, Tagami[16] reported that Mg contamination from MgO crucible is only about 0.02 wt% for the same composition. This difference in the impurity level should alter the phase diagram. In other words, Al contamination probably leads to the decrease of the peritectic temperature of Pr247 and Pr124. Further, Al ion prefers to substitute for Cu in the single chain, but not in the double chain.[17] Therefore, 247 and 123 phases are expected to grow easier in the presence of Al impurities.

A SEM image of one of the Pr124 single crystals is shown in Fig. 5(a). The size of this crystal was approximately $2\times0.4\times0.04\ \mathrm{mm}^3$, which is the largest of the Pr124 crystals grown in this study. The shape of the crystal is rectangular, and the surface is very smooth. Most of the other Pr124 crystals are similar in the shape. The x-ray diffraction study revealed that the surface is the ab plane, and no impurity phase was detected. Figure 5(b) is a photograph of the $(hk0)$ reciprocal plane taken with a x-ray precession camera with the incident beam along the (001) direction. The result shown in Fig. 5(b) together with a similar result obtained with the incident beam along the (100) direction indicates that the crystal is free from twins and consists of a single grain. In addition, this crystal was found to be orthorhombic with the space group *Ammm* and lattice parameters of $a = 3.881(4)$ Å, $b = 3.900(2)$ Å, and $c = 27.42(3)$ Å, being consistent with the result of the study on polycrystalline Pr124.[13] The long edge of the crystal in Fig. 5(a) is the b-axis direction (// chain). Using this sample as a standard, the crystallographic axes of the other crystals were determined with a polarizing microscope. In most Pr124 crystals, the longer edge was parallel to the b-axis direction, probably because the as-grown Pr124 crystals are orthorhombic, and an anisotropic growth have taken during the synthesis. Such anisotropic growth in the ab plane is not observed for the 123 phase due to the tetragonality of as-grown crystals. The composition of the Pr124 crystal analyzed by the techniques described in Sec. II was $PrBa_{1.97}Cu_{3.96}Mg_{0.04}O_8$. Mg is reported to substitute preferentially for Cu in the CuO_2 plane in Y123.[6] Supposing that all Mg impurities go similarly into the CuO_2 plane in Pr124, it means that 2 at% of Cu in each layer is substituted by Mg.

A SEM image of one of the Pr247 single crystals is shown in Fig. 6(a). The size of this crystal was approximately $0.3\times0.5\times0.04\ \mathrm{mm}^3$. This crystal has a plate shape and the surface is rather rough with many steps. The x-ray diffraction study revealed that the surface is the ab plane, and no impurity phase was detected. The $(hk0)$ reciprocal plane observed using a x-ray precession camera is shown in Fig. 6(b). This result indicates that the crystal is free from twins and apparently consists of a single grain. However, the $(h0l)$ reflections observed with the incident beam along the (010) direction revealed circumferentially streaked spots, which suggests that the growth along the b-axis direction contains small fluctuation. The lattice parameters of the

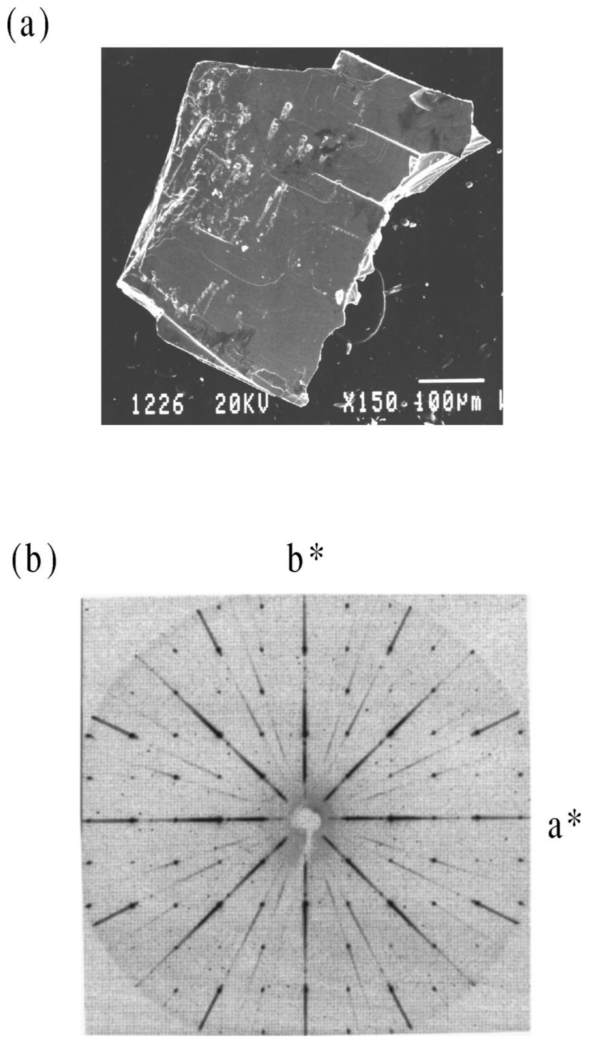

FIG. 6. A SEM image (a) and a $(hk0)$ precession pattern (b) of one of the Pr247 single crystals.

Pr247 single crystal are found to be $a=3.864(4)$ Å, $b=3.900(2)$ Å, and $c=50.28(3)$ Å, showing a larger orthorhombicity and a shorter *c*-axis length than polycrystalline Pr247.[13] The origin of these differences may be attributed to oxygen deficiency and/or substitution effect of Al for Cu in the single crystal. Pr247 single crystals grown in Al_2O_3 crucibles were rather irregular in shape as shown in Fig. 6(a) and the surface tends to be rough. Such imperfectness in crystal shape can seriously affect the results of transport measurements in a strongly anisotropic material like Pr247. Therefore, in the study of transport measurements reported below, we focused only on Pr124 crystals grown in MgO crucibles, which were rectangular in the shape and had smooth surfaces.[18]

C. Anisotropic resistivity of Pr124 single crystal

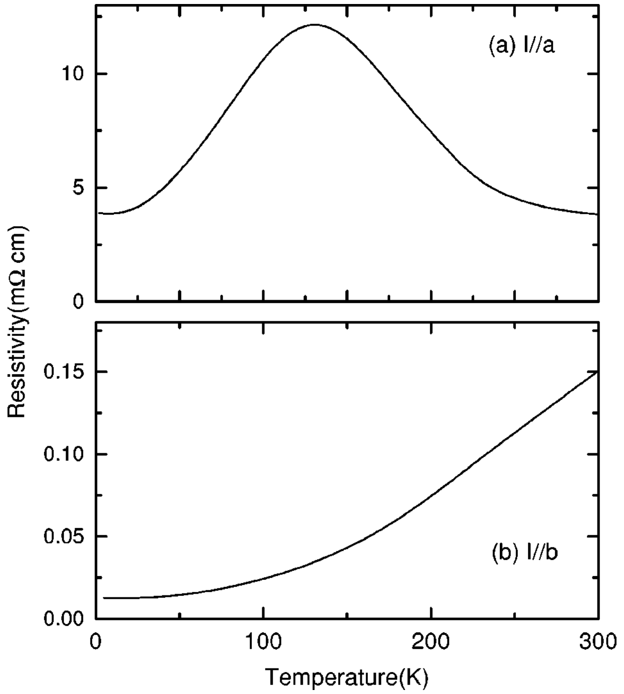

FIG. 7. Temperature dependence of resistivities of Pr124 single crystal along the *a* (a) and *b* axes (b), respectively.

Using the Pr124 single crystals grown in MgO crucibles, we measured the temperature dependence of resistivity along *a*- and *b*-axis directions. Superconductivity was not detected down to 2 K for the measured forty single crystals. As shown in Fig. 7(a), the temperature dependence of resistivity along the *a*-axis ($\perp$ chain) direction (ρ_a) possesses a maximum at about 140 K. The value of ρ_a is about 4 mΩ cm at room temperature, indicating that the numbers of mobile carriers within the CuO_2 plane is obviously less than that of optimally doped high-temperature superconductors. The resistivity along the *a*-axis direction increases with decreasing temperature (negative TCR) from room temperature down to 140 K, and exceeds 12 mΩcm. However, ρ_a then starts to decrease below 140 K (positive TCR), becomes about 4 mΩ cm at 2 K. This behavior was reproduced in all crystals, for which ρ_a was measured.

Figure 7(b) shows the temperature dependence of resistivity measured along the *b*-axis (// chain) direction (ρ_b). The values of ρ_b of all measured twenty crystals ranged from 100 $\mu\Omega$ cm to 150 $\mu\Omega$ cm at room temperature. This value is in good agreement with the resistivity along the double chain site of Y124 single crystals as reported by Hussey *et al.*[19] On the other hand, the temperature dependence of the measured ρ_b was sensitively affected by an even slight misalignment of the voltage electrodes because of the large anisotropy in resistivity. For instance, some crystals showed a localizationlike behavior at low temperatures and some exhibited a resistance peak at about 140 K. However, these behaviors were poor in reproducibility, and must have resulted from voltage drops along the *c*- and *a*-axes, respectively, due to imperfectness in the crystal shape. We checked carefully the reproducibility, and conclude that the intrinsic behavior along the *b*-axis direction is metallic in the whole temperature range up to 300 K, as shown in Fig. 7(b). The metallic behavior indicates the presence of a finite density of states at the Fermi energy in Pr124. In addition, the large anisotropy in resistivity between the *a*- and *b*-axes strongly suggests that the metallic behavior along the *b*-axis direction originates from the double chain site. The temperature dependence of $1/(\rho_a^{-1}-\rho_b^{-1})$ did not follow the T^2 dependence near room temperature, which was claimed for the Y systems.[3,4]

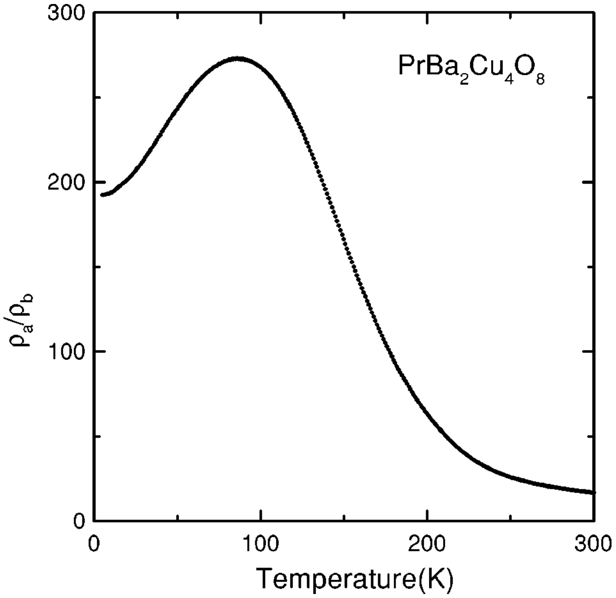

FIG. 8. Temperature dependence of ρ_a/ρ_b of Pr124 single crystal.

It is also important to study the behavior of *c*-axis conduction in the relation with the interchain interaction along this crystallographic direction as Hussey *et al.* pointed out in their work on Y124.[20] However, although we measured thoroughly and carefully the resistivity along *c*-axis for many samples using a quasi-Montgomery method, the results were poor in reproducibility, especially at low temperatures. This is probably because the samples are too thin and are highly anisotropic. Therefore, the intrinsic behavior of *c*-axis conduction in Pr124 requires further studies.

Figure 8 shows the anisotropy of the resistivity as a function of temperature. The in-plane anisotropy, ρ_a/ρ_b, is about 20 at room temperature, increases with decreasing temperature, and exceeds 200 below 130 K. Therefore, the electronic conduction in Pr124 is highly anisotropic at low temperatures. There are at least two possibilities for the origin of the peak in the ρ_a-T curve. One is that ρ_a reflects the conduction only along the CuO$_2$ plane in the whole temperature range. In this case, the peak must have its origin in the CuO$_2$ plane. The second possibility is that interchain conduction across Cu-O chains becomes allowed at low temperatures, while CuO$_2$ layer remains essentially semiconductive, and the peak indicates the switching between these two sites as the dominant conduction path. Terasaki *et al.* have proposed that Pr124 undergoes a dimensional crossover at about 100 K by lowering the temperature, and the conduction becomes 2D at low temperature.[14] The presence of a similar dimensional crossover have been argued for quasi-1D organic conductors.[21] If the conduction along the CuO$_2$ plane can be neglected at low temperature in Pr124, we can estimate the ratio of the transfer integral along the double chain to that across the chains, $t_{\mathrm{chain}}/t_{\mathrm{inter\text{-}chain}}$, to be about 14, using the formula $\rho/\rho' \propto (t/t')^2$. This value is consistent with that estimated by Terasaki *et al.*[14] To shed more light on the relation with the peak in the ρ_a-T curve and the proposed dimensional crossover, however, further studies on single crystals are necessary, like transport measurement in magnetic field, and/or pressure dependence of the ρ_a-T curve, which would be the subject of a near future work.

Finally, we would like to comment on the absence of superconductivity in Pr124. Recently, superconductivity was reported for Pr123 in single crystals prepared by the travelling solvent floating zone method or in sputtered thin film with $T_c = 80$ K (Ref. 22) and 76 K (Ref. 23), respectively. On the other hand, Tagami and Shiohara[24] grew Pr$_{1-z}$Ba$_{2+z}$Cu$_3$O$_7$ single crystals with $z = 0.01-0.29$ by the crystal-pulling method and found that the resistivity of the crystal with $z = 0.01$ is three orders of magnitude smaller than that with $z = 0.29$ at room temperature, but found no indication of superconductivity. As described above, our Pr124 crystals contain small amounts of Mg. The reported result of Y123 indicates that substituting Mg for 2% of Cu in the CuO$_2$ planes lowers T_c from 91 K to 72 K, but it is not enough to completely destroy superconductivity.[25] Further, our previous Rietveld refinement of neutron diffraction patterns measured on Pr124 polycrystalline samples showed that Pr ions are hardly substituted for Ba in Pr124.[13] Moreover, the results of thermogravimetry measurement on polycrystalline samples indicated that oxygen is very stable in Pr124 up to 800 °C. Therefore, it is very unlikely that either substitution of Pr for Ba, oxygen deficiency or impurities caused the absence of superconductivity in our Pr124 crystals. Zou *et al.* reported that when the *c*-axis lengths are plotted as a function of R^{3+} (R=Y or rare earth elements) ionic radius, superconducting Pr123 lies on the curve that was drawn through the data of other RBa$_2$Cu$_3$O$_7$, while nonsuperconducting Pr123 has a substantially shorter *c*-axis length.[22] We made a similar check for our crystals, and found that the *c*-axis length of the crystals is well consistent with the extrapolation of the published data[26] of RBa$_2$Cu$_4$O$_8$ polycrystalline samples. Therefore, we believe that Pr124 is not a superconductor, even in case that the *c*-axis length is sufficiently large.

IV. CONCLUSION

We have successfully prepared Pr247 and Pr124 single crystals by means of a flux method under 11 atm of pure oxygen gas using Al$_2$O$_3$ and MgO crucibles. The growth of the crystals was possible even though both phases are not adjacent to the liquid phase on the phase diagram. The success of the crystal growth was achieved by thoroughly studying the starting composition dependence of the generated phases and by skipping the high-temperature stable phases with a rapid cooling step during the heat treatment. The electronic conduction of the Pr124 single crystal was found to be extremely anisotropic with the highest conductivity along the *b*-axis direction, i.e., along the double chain site.

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