Superconducting behaviours in reduction-treated mixtures of fine Pr124 and Pr123 ceramics

K Koyama¹, R Nakashima¹, K Magishi¹, T Saito¹, T Shima² and M Hagiwara²

¹Institute of Socio-Arts and Sciences, The University of Tokushima, Tokushima 770-8502, Japan
²Faculty of Engineering and Design, Kyoto Institute of Technology, Kyoto 606-8585, Japan

E-mail: koyama@ias.tokushima-u.ac.jp

Abstract. Superconducting behaviours in reduction-treated mixtures of fine Pr124 and Pr123 ceramics synthesized using citrate pyrolysis precursor method are examined by electrical resistivity and magnetic measurements. With increasing the ratio of Pr123, the temperature dependence of \( \rho(T) \) changes to be semiconductor-like behaviour hugely, and there exist no broad maximum for as-sintered Pr124/Pr123 (1:1.5) and (1:2) samples contrary with the case of (1:1). By reduction treatment, the \( \rho(T) \) curve shows the maximum according to the increase of carrier concentration in the CuO double chain in Pr 124 grains. By subtracting the Pr\(^{3+}\) paramagnetic contribution from the temperature dependence of magnetization, the remnant magnetization shows weak diamagnetism below \(~17\) K, indicating small Meissner effect. The diamagnetic susceptibility is independent of magnetic field in the measured field range below 20 Oe.

1. Introduction

For Y-base cuprate superconductors, Pr substitution for Y sites restrains the CuO\(_2\) plane conductivity. So, possible superconductive nature at CuO double chains can be searched experimentally in such Pr-substituted materials. As known, the compounds include several related phases distinguished by layered pattern of crystalline blocks of CuO double chain (-D-) and/or single chain (-S-), alongside of CuO\(_2\) plane. In these, Pr\(_2\)Ba\(_4\)Cu\(_7\)O\(_{15-}\delta\) (Pr247) has been found to show electron-doped superconductivity at -D block when the ceramic was reduction treated [1,2]. Then Pr247 has being regarded as an essential studying material bringing new viewpoints of cuprate oxide superconductors.

Citrate pyrolysis (CP) is a method to produce reactive precursor for syntheses of oxide compounds [3]. From the precursor, many kinds of oxide superconductors can be synthesized by each single calcination process at ambient pressure condition. Rather variable sintering condition in this method may have been utilized not only to our experimental study of inter-grain ordering in ceramic superconductors [4] but also to prepare Pr\(_2\)Ba\(_4\)Cu\(_7\)O\(_{15-}\delta\) (Pr247) ceramic superconductors [5], and furthermore, may be applicable to prepare multi-phase mixed fine ceramic systems.

Recently, superconductive characteristics of multi-phased ceramic samples consist simply of PrBa\(_2\)Cu\(_4\)O\(_y\) (Pr124) and PrBa\(_2\)Cu\(_4\)O\(_{7-}\delta\) (Pr123) with different ratio prepared by citrate pyrolysis (CP) method [6] are examined experimentally. After reduction treatment by vacuum-heating at 450°C, the
multi-phased samples of Pr124+Pr123 (1:1) and (2:1) show onset of abrupt electrical resistivity dropping and also weak Meissner magnetization below ~20 K. The results suggest that superconductivity at CuO double chains in Pr124 grains is caused by charge (electron) transfer from neighboring Pr123 grains. [7,8]

The increase of Pr 123 grain (source of electron supply) ratio is expected to enhance the inter-grain charge transfer effect from Pr123 to Pr124 submicron grains of mixed ceramics by reduction treatment. In the present work, superconductive signs in electrical resistivity and magnetic behaviours of mixed ceramic samples with the ratio of Pr124 : Pr123 = 1:1.5 and 1:2 are searched and discussed, to advance preceding discussion about the superconductive region induced by inter-grain charge (electron) transfer effect.

2. Samples and experiments
An intentionally multi-phased ceramic sample composed purely of Pr124 and Pr123 was synthesized by the mix-sintering method. For this method, various mass ratios of pure calcined powders of Pr124 and Pr123 were prepared independently by the citrate pyrolysis (CP) precursor method at the respective conditions. Then various mass ratios of these (Pr124:Pr123 = 1:1, 1:1.5 and 1:2) were mix-grinded and pressed, and was sintered at 870°C (below the formation temperatures of both Pr124, Pr247 and Pr123). Judged from the XRD observation, the obtained samples consist simply of Pr124 and Pr123, except for a little impurity of BaCuO2 and PrBaO3 formed at the calcinations. Seen from TEM experiments, no Pr247 structure is formed anywhere in the samples within sampling tries.

Pieces of these ceramic samples were vacuum-heated for 24 h at 300-550°C to be various reduction grade samples. In the present work, the reduction treatments were done at 350°C and 400°C for the mix-sintered samples of Pr124:Pr123 = 1:1.5 and 1:2, respectively. Attained oxygen reduction degree was estimated by measuring weight loss % (δwt%) of the pieces.

Electrical resistivities were measured in temperature range 4-300 K. AC 4-wire method by lock-in amplifying was applied using ac current of 23.0 Hz, 1-10 mA. Temperature dependence of DC magnetization was measured by Quantum Design’s MPMS with SQUID magnetometer for both reduced and as-sintered (O2 annealed) samples.

3. Results and discussion

3.1. Electrical resistivity measurements
At first, temperature dependences of electrical resistivity for the as-sintered multi-phased Pr124+Pr123 (1:1, 1:1.5 and 1:2) samples are compared as shown in Figure 1. With increasing the ratio of Pr123,
Resistivities vs. temperature for as-sintered and reduced mixed ceramic samples of Pr124+Pr123 with the ratio of (a) (1:1) and (b) (1:2).

The temperature dependence of $\rho(T)$ changes to be semiconductor-like behaviour hugely contrary with the metallic behaviour in the Pr124+Pr123 (1:1) sample below 150K. There exist no broad maximum for Pr124+Pr123 (1:1.5) and (1:2) samples as observed in the case of (1:1). [7,8] This is considered to be the semiconductive nature of Pr123 phase is dominant comparing with the metallic behaviour of CuO double chain in Pr124 phase also in low temperature region. It is quite different with the previous result of Pr124+Pr123 (1:1). [7,8]

Reduction effects on $\rho(T)$ curve for the Pr124+Pr123 (1:1) sample is shown in Figure 2(a).[7] The curve of as-sintered sample shapes broad maximum at about 150K similar to the simple Pr247. As for the reduced sample of $\delta_{\text{wt\%}}=0.835$ (vacuum-heated for 24h at 450°C), the $\rho(T)$ curve shows delicate but meaningful characteristics; the maximum shifts a little toward higher temperature, and rather steep drop is revealed around about 20K. Reduction effects on $\rho(T)$ curve for the Pr124+Pr123 (1:2) sample is shown as comparison with the as-sintered one in Figure 2(b). The curve of as-sintered sample is semiconductor-like behaviour in all temperature range. As for the reduced sample of $\delta_{\text{wt\%}}=0.996$ (reduced temperature: 350°C), the $\rho(T)$ curve shows the maximum at about 50K. With increasing the reduced treatment temperature, the maximum temperature of $\rho(T)$ curve increases slightly to 80K for the 400°C reduced sample in spite of almost the same $\delta_{\text{wt\%}}$ value with that for 350°C reduced one. This is according to the increase of carrier concentration in the CuO double chain in Pr 124 grains, and shows the weak metallic behaviour below the $\rho(T)$ maximum temperature.

The result for the reduction effects for the sample of Pr124+Pr123 (1:1.5) is similar to that for the Pr124+Pr123 (1:2). However, any kinds of resistivity dropping just like the case of the reduced Pr124+Pr123 (1:1) sample at 450°C [7,8] are not observed in both Pr124+Pr123 (1:2) and (1:1.5) samples reduced below 400°C. The carrier transfer effect from Pr123 grain to the CuO double chain in Pr 124 grain may not be enough in these reduction treatment conditions.

3.2. Magnetic measurements

Peculiar magnetic behaviour reflected by the superconductive(-like) contribution is then discussed. DC field-cooling magnetizations for the reduced Pr124+Pr123 (1:2) sample (reduced temperature: 350°C) under the magnetic field of H=0.4 Oe and 16 Oe are shown against temperature in Figure 3(a) and (b), respectively. Main part of magnetization is considered to be from Pr$^{3+}$ paramagnetic contribution, which is estimated as Curie-Weiss law (fitting by using the experimental data above 20K), as shown by dotted line in the figures. Besides, magnetization increases abruptly below 12K, indicating the ferromagnetic spontaneous component caused by the impurity PrBaO$_3$ phase. [9]
The amount of increase by ferromagnetic moment are almost independent of magnetic field. The weak diamagnetic component is distinctly observed below ~17 K as the discrepancy from the Curie-Weiss fitting curve of paramagnetic Pr$^{3+}$.

The Curie-Weiss parameters are estimated in Figure 4. The Curie constant C and residual susceptibility $\chi_0$ are estimated as gradient of Figures 4(a) and 4(b), respectively. From the value of Curie constant, the effective number of Bohr magneton is estimated as about 3.2, comparing with the theoretical value of 3.58 for Pr$^{3+}$ ion. The Curie Weiss temperature $\theta$ is about 7K, and independent of magnetic field. As the result, the paramagnetic susceptibility of Pr$^{3+}$ ions in both Pr124 and Pr123 grains are considered as ordinary behavior.

By subtracting the Pr$^{3+}$ paramagnetic contribution, the difference between experimental magnetic moment and Pr$^{3+}$ paramagnetic moment $\Delta M (= M_{\text{exp}} - M_{\text{para}})$ is plotted against temperature as shown in Figure 5(a) under $H=0.4$ Oe and 5(b) $H=16$ Oe, respectively. $\Delta M$ shows weak diamagnetism below
Figure 5. ΔM after subtraction of Pr$^{3+}$ paramagnetic contribution vs. temperature for 350°C-reduced mixed ceramic sample of Pr124+Pr123 (1:2) under the field of (a) 0.4 Oe and (b) 16 Oe, respectively.

~17 K, indicating small Meissner effect, but changes abruptly toward positive value below 12 K, implying spontaneous magnetic moment. A small impurity PrBaO$_3$ is considered as the ferromagnetic origin.[9] Ferromagnetic spontaneous component is almost independent on magnetic field. The other hand, the diamagnetic component increases with magnetic field strength. Moreover, the effect of another paramagnetic impurity (BaCuO$_2$ or other impurities) becomes remarkable in the low temperature and strong magnetic field region.

In order to neglect the effect of ferromagnetic ordering of impurity PrBaO$_3$ below 12K, the amounts of ΔM against temperature above 12K are shown as in Figure 6 under various magnetic field.

Figure 6. ΔM against temperature above 12K under various magnetic field for the 350°C -reduced Pr124/Pr123 (1:2) sample.

Figure 7. Magnetic field dependence of diamagnetism ΔM at 12K for the 350°C -reduced Pr124/Pr123 (1:2) sample.
for the 350°C-reduced Pr124/Pr123 (1:2) sample. The onset temperature of small diamagnetism caused by Meissner effect is about 17K. The diamagnetic moment increases with increasing magnetic field in the measured field region. The magnetic field dependence of diamagnetism $\Delta M$ at 12K (without the influence of ferromagnetic impurity PrBaO$_3$) is shown as in Figure 7. The diamagnetic susceptibility is constant below 16Oe. However, estimated Meissner volume fraction is considered as quite small (about 0.1%). This is because the inter-grain charge transfer effect from Pr123 to Pr124 grains is considered to be occurred in the quite small region in the sample. The other possibility is that the appearance of charge in Pr123 grain is not enough by the reduction treatment below 400°C in the present study.

4. Conclusion
Reduction treatments in vacuum for 24 h below 400°C for the mixed ceramic samples with the ratio of Pr124 : Pr 123 = 1:2 and 1:1.5 bring the appearance of broad maximum in $\rho(T)$ curve. This is considered to be caused by the inter-grain charge transfer effect from CuO single chain site of Pr123 grains to CuO double chain site of Pr124 grains. By subtracting paramagnetic component of Pr$^{3+}$ ions, ferromagnetic trace below 12K of impurity phase PrBaO$_3$ and diamagnetic Meissner signal is observed in the same sample below 17 K, just like the previous result for the Pr124 : Pr 123 = 1:1 sample reduced at 450°C. The inter-grain charge transfer effects not only in the mixed samples with different Pr124:Pr123 ratio but also reduced at higher temperature are now on progress.

References
[1] Matsukawa M, Yamada Y, Chiba M, Ogasawara H, Shibata T, Matsushita A and Takano Y 2004 Physica C 411 101
[2] Yamada Y and Matsushita A 2005 Physica C 426-431 213, and the references therein
[3] Koyama K, Junod A, Graf T, Triscone and G, Muller J 1991 Physica C 185-189 461
[4] Yamao T, Hagiwara M, Koyama K and Matsuura M 1999 J. Phys. Soc. Jpn. 68 871
[5] Hagiwara M, Shima T, Tanaka S, Nishio K, Isshiki T, Saito T and Koyama K 2007 Physica C 463-465 161
[6] Hagiwara M, Shima T, Shugano T, Koyama K and Matsuura M 2006 Physica C 445-448 111
[7] Hagiwara M, Kitada R, Shima T, Nishio K, Kanda S, Deguchi H, Koyama K and Matsuura M 2009 J. Phys.: Conf. Series 150 052065
[8] Hagiwara M, Shima Tanaka S and Koyama K 2010 Physica 470 S65
[9] Felner I et al. Phys. Rev. 1992 B 46 9132