Superconductive Transition and the Intergrain Effects of Mixture Ceramic Systems Synthesized using Citrate Pyrolysis Precursor Method

M Hagiwara¹, R Kitada¹, T Shima¹, K Nishio¹, H Deguchi², K Koyama³ and M Matsuura⁴

¹Department of Electronics, Kyoto Institute of Technology, Kyoto, 606-8585, Japan
²Faculty of Engineering, Kyushu Institute of Technology, Kitakyushu 804-8550, Japan
³Faculty of Integrated Arts and Sciences, The University of Tokushima, Tokushima 770-8502, Japan
⁴Fukui University of Technology, Fukui 910-8505, Japan

E-mail: hag@kit.ac.jp

Abstract. Superconductive characteristics of Pr$_2$Ba$_4$Cu$_7$O$_{15-\delta}$ (Pr247) ceramics with crystalline phase inhomogeneity for the stacking structures is examined experimentally, using reference observations for multi-phased ceramic sample consists simply of PrBa$_2$Cu$_4$O$_8$ (Pr124) and PrBa$_2$Cu$_3$O$_{7-\delta}$ (Pr123). After reduction treatment by vacuum-heating, the reference multi-phased sample shows onset of abrupt electric 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 transfer from neighbouring Pr123 grains. Such a charge transfer effect is thought to occur also in Pr247 sample including phase inhomogeneity.

1. Introduction

Citrate pyrolysis (CP) is a method to produce reactive precursor for syntheses of oxide compounds [1]. 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 also utilized to our experimental study of intergrain ordering in ceramic superconductors [2,3], and further, may be applicable to prepare multi-phase mixed ceramic systems. Recently the authors have applied the method to prepare Pr-series superconductor [4,5].

It had been recognized that Pr substitution for Y sites in Y-base cuprate superconductors restrains the CuO$_2$ plane conductivity [6], so that conductive nature at CuO chains in the crystal can be studied experimentally. A recent notable finding was that superconductivity is brought by the CuO double chains (−D−) of Pr$_2$Ba$_4$Cu$_7$O$_{15-\delta}$ (Pr247) of which the sintered material was reduction-treated.[7,8] Then Pr247 has being regarded as an interesting material of electron-doped superconductivity at one-dimensional −D− chains.

In the authors’ preceding experiments for the Pr247 prepared by CP method, superconductivity by the reduction was confirmed, and the critical temperature $T_c$ was found to be about 10 K higher than reported value in Refs. 6 and 7.[4] At the same time, the Pr247 samples were found to contain Pr124 phase and stacking fault region rich in CuO single chain (−S−), with the help of X-ray diffraction.
(XRD) and transmission electron microscopy (TEM) observations.[4] Then, it has been speculated that oxygen-reduction at the $-S-$ rich region may affect superconductive carrier doping to $-D-$ chains at Pr247 region or possibly at Pr124 region over the grain boundaries.[4,5]

For further discussion, in this work, the ceramic Pr247 samples with different structural purity are examined comparatively. And a new reference specimen is synthesized as a simply mixed ceramic of Pr124 and Pr123, in order to clarify the possibility of superconductivity by Pr124 structure in our ceramic Pr247 material.

2. Samples and experiments
As a characteristic of our synthetic method using ambient pressure condition, it is hard to create pure Pr247 of uniform stacking structure.[4] However, a ceramic of purer Pr247 has been rarely obtained, with the help of many trials of calcinations. So, a typical multi phase sample (named I) and nearly single phase one (named II) are taken up comparatively. It is confirmed by XRD that about 20 wt% Pr124 phase is included in the sample I, and that such phase complexity is absent for the sample II. By TEM experiments, some irregular stacking patterns rich in $-S-$ is detected for the sample I.

Besides, an intentionally multi-phased ceramic sample (named III) composed purely of Pr124 and Pr123 was synthesized by the mix-sintering method. For this method, an equal mass of pure calcined powders of Pr124 and Pr123 were prepared independently at the respective conditions. Then an equal mass of these was mix-grinded and pressed, and was sintered at 870°C (below formation conditions of both Pr124 and 123). Judged from the XRD observation, the obtained sample III consists simply of Pr124 and 123, except for a little impurity of BaCuO$_2$ and PrBaO$_3$ formed at the calcinations. Seen from TEM experiments, no Pr247 structure is formed anywhere in this sample within sampling tries.

Pieces of these ceramic samples were vacuum-heated for 24 h at 300-550°C to be various reduction grade samples for I or II. As for the mix-sintered sample III, the treatment was done at 450°C for 24 h. Attained oxygen reduction degree was estimated by measuring weight loss % ($\delta_{\text{wt}}\%$) of the pieces.

Electric resistivities were measured in temperature range 5-300 K. AC 4-wire method by lock-in amplifying was applied using ac current of 8.0 Hz, 5.0-10 mA. Temperature dependence of DC magnetization was measured with SQUID magnetometer for the reduced piece of sample III.

3. Results and discussion
Superconductive transitions caused by reduction for the serieses I and II have been compared using their resistivity results.[5] Superconductive onset temperatures ($T_{\text{on}}$) estimated as cross points of the asymptotic lines of each dropping $\rho(T)$ curve from normal-conducting side and from lower temperature side, and then are plotted against $\delta_{\text{wt}}\%$ for both I and II in Figure 1 (where such estimations

**Figure 1.** Superconducting onset temperature vs. $\delta_{\text{wt}}\%$ for Pr247 sample series I and II. The values are estimated regardless whether zero-resistivity is attained or not.

**Figure 2.** Schematic explanation of difference between homogeneous stacking structure for pure Pr247 (a), and decomposed structure for multi phase sample (b). (The figures do not represent real structural views.)
have been carried out regardless whether zero-resistivity is attained or not. \( T_{\text{con}} \) is relevant indication of intragrain superconducting transition point, for our ceramics behave as intergrain junction systems.\[4\] \( T_{\text{con}} \) of the sample series I arises at critical region of \( \delta_{\text{wt\%}} \) between 0.2 and 0.3, while \( T_{\text{con}} \) of II arises at \( \delta_{\text{wt\%}} \) between 0.3 and 0.4. Maximum \( T_{\text{con}} \) caused by enough large \( \delta_{\text{wt\%}} \) is \( \sim 25 \text{ K} \) for both (or possibly a little smaller for II than I). It is noted here that purer sample II requires rather larger reduction degree \( \delta_{\text{wt\%}} \) than I.

We should now confirm meaning of \( \delta_{\text{wt\%}} \) in the multi phase sample. As known, Pr124, Pr247 and Pr123 are associated compounds in which crystallographic layered pattern of \( -D- \) and \( -S- \) is different. Since elemental component \( \text{Pr:Ba:Cu}=2:4:7 \) \((=124+123)\) is fixed in our samples, actually possible inhomogeneity is regarded as replaced arrangement of \( -D- \) and \( -S- \) from Pr247 structure (Figure 2). If equivalent oxygen deficient ratio is assumed for any \( -S- \) in a reduced sample, observed \( \delta_{\text{wt\%}} \) can also represent oxygen deficiency at Pr247 region in the sample. \((0.947 \delta_{\text{wt\%}} \text{ corresponds to } \delta \text{ in the expression Pr}_2\text{Ba}_4\text{Cu}_7\text{O}_{15-\delta} \text{ when the reduction occurs exactly from } \delta=0)\). Thus the parameter \( \delta_{\text{wt\%}} \) is valid even for samples I and II. Considering this, the result of Figure 1 does not mean difference of effective reduction degree of Pr247 in I and II, but suggests more essential occurrence in the multi phase sample I. Superconductive contribution of \( -D- \) outside of Pr247 region is then speculated.

In order to know what occurs intrinsically in multi phase ceramic without Pr247, sample III as a sintered multi-phased Pr124/Pr123 is examined experimentally. Reduction effects to \( \rho(T) \) curve for the sample III is shown in Figure 3. The curve of as-sintered state shapes round peak like simple Pr247. As for the reduced sample of \( \delta_{\text{wt\%}}=0.835 \), the \( \rho(T) \) curve shows delicate but meaningful characteristics; the maximum shifts a little toward higher temperature, and rather steep drop is revealed around the lower temperature side. However, the dropping tends to stagnate and does not reach zero-resistivity. We notice that such a kind of resistivity dropping had been often seen in mixture materials containing a little amount of superconductive phase. Seen in the enlarged view (Figure 4), apparent \( T_{\text{con}} \) is read to be \( \sim 20.8 \text{ K} \) (with the same rule for samples I and II). Though this value is smaller than attainable \( T_{\text{con}} \) value in Figure 1 for sample I or II, the difference is not so large.

On the assumption that the partial superconductivity is realized, a possible origin will be considered. Firstly suspected a little Pr247 formation in the sample III is almost denied by our TEM result (in §2). Then in the reduced system of the multi-phased Pr124/Pr123, \( -D- \) chain in Pr124 region is probably the only candidate for the superconductive origin, considering Pr-substitution effect to \( \text{Cu}_2\text{O}_2 \) plains and oxygen defects at \( -S- \) chains. We may speculate, therefore, that oxygen reduction at \( -S- \) of Pr123 grains contribute to superconductive electron doping to \( -D- \) in the neighboring Pr124 grains through the boundaries.

---

**Figure 3.** Resistivities vs. temperature for mix-sintered ceramic of Pr124/Pr123 (sample III) of as-sintered state and reduction-treated state.

**Figure 4.** Enlarged view of the abrupt resistivity dropping for the reduction treated sample III in Figure 3.
Such a speculation appears to contradict the fact of unattainable zero-resistivity, since volume ratio of the 124 parts in the sample III believed to exceed ‘per colation limit’ value expected in this case (0.25 for cubic array [9]). However, this problem is understandable when we consider as follows. Mutual contact of Pr124 and Pr123 grains is thought to be incomplete in the ceramic, so a small part of Pr124 grains may show superconductivity.

Peculiar magnetic behaviors reflected by the superconductive(-like) contribution is then discussed. DC field-cooling magnetization ($M_{FC}$) and thermo-remnant one ($M_r$) after the cooling at 0.1 Oe are shown against $T$ in Figure 5. $M_{FC}$ shows weak diamagnetism below $\sim$17 K, indicating small Meissner effect, but it turns the sign suddenly and rises toward positive direction below $\sim$12 K. Besides, $M_t$ decreases abruptly around 12 K, but remains small positive tail vanishing around 17 K. While these behaviors seem to be concerned with the superconductive grains and their intergrain ordering, the mechanism is not clear in this stage. We now speculate, however, as follows. Superconductive Pr124 grains are formed sparsely and inhomogeneously, so that only a few isolated intergrain small clusters may exist in the ceramic. At $\sim$12 K of the intergrain ordering, random local magnetic moments by the spontaneous loop current arises, and they behave elements of paramagnetic-Meissner effect [10].

To summarize, suggestive information has been derived about the superconductive nature of our Pr247 ceramics including phase inhomogeneity. A reference ceramic of reduced multi-phased Pr124/Pr123 shows characteristic behavior probably caused by small amount of superconductive grains, though it does not reach zero-resistivity. This result suggests that superconductivity at $\sim$D$-$ in Pr124 is caused by reduction at $\sim$S$-$ in the neighbouring Pr123 grains. And such a charge transfer effect might occur also in our earlier reported Pr247 sample. In order to confirm the possibility, superconductive region is tried to be increased in the mix-sintered sample by some improvement of mortar and homogenization, to pursue zero-resistivity and quantitatively reasonable Meissner ratio.

The authors express finally that this work was supported by both Grant-in-Aid for Exploratory Research (40655001) and Grant-in-Aid for Scientific Research on Priority Areas (19052006).

References
[1] Koyama K, Junod A, Graf T, Triscone and G, Muller J Physica C 185-189 461
[2] Kawachi M, Hagiwara M, Koyama K and Matsuura M, J. Phys. Soc. Jpn. 63 3405
[3] Yamao T, Hagiwara M, Koyama K and Matsuura M, J. Phys. Soc. Jpn. 68 871
[4] Hagiwara M, Shima T, Tanaka S, Nishio K, Ishihiki T, Saito T and Koyama K Physica C 463-465 161, and the references therein
[5] Hagiwara M, Tanaka S, Shima T, Gotoh K, Kanda S, Saito T and Koyama K Physica C in press
[6] Tanaka M, Tanaka T, Sakata T, Sasaki S, Kodama K and Sato M Physica C 263 340
[7] Matsukawa M, Yamada Y, Chiba M, Ogasawara H, Shibata T, Matsushita A and Takano Y Physica C 411 101
[8] Yamada Y and Matsushita A Physica C 426-431 213, and the references therein
[9] Yonezawa F, Sakamoto S and, Hori M Phys. Rev. B 40 636
[10] Braunish W, et al. Phys. Rev. B 48 4030, and the references therein