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Oxidation and reduction effects of successive superconducting transitions in ultra-fine $YBa_2Cu_4O_8$ ceramics

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Abstract. We investigated the effects of oxidation and reduction on the successive superconducting transition in a ceramic material composed of $YBa_2Cu_4O_8$ (Y124) submicron grains by linear and non-linear resistivity measurements. This material shows two-step superconducting transition and the lower one is identified as an inter-grain ordering. A sintering process fuses and joins the adjacent grains, so the lower transition was suppressed with increasing sintered time. Although Y124 is a stoichiometric ceramic, a reduction treatment suppressed the temperature of zero resistivity and broadened the non-linear resistivity peak. This suggests an oxygen vacancy was induced on the grain surface.

1. Introduction

The ceramics system composed of submicron superconductive grains has been studied focusing on the transition process from intra-grain to inter-grain orderings. It forms a Josephson-coupled inter-grain network and a novel ordering phenomenon such as a chiral glass transition is expected. [1]

A ceramic material of stoichiometric superconductor $YBa_2Cu_4O_8$ (Y124) shows successive two-step superconducting transition. [2] Y124 is composed of the superconducting CuO_2 planes and the edge-sharing CuO double chains which are stable and considered to be free from microscopic randomness due to the oxygen vacancy. The temperature dependence of the electrical resistivity $\rho(T)$ shows a rapid drop at about 80 K but it decreases gently with decreasing temperature below 76 K, and then reaches zero at around 27 K. [3] The upper transition was identified as the intra-grain superconductive ordering, and the lower one was identified as the inter-grain ordering. These features are in agreement with the magnetic measurements. [2]

The inter-grain transition is characterized by a random Josephson-coupled network containing the so-called π junctions. The zero resistivity temperature depends on the sintering condition, which suggests the circumstance of the inter-grain boundary can be changed by the sintering treatment. [2]

Recently, the authors found that the lower transition is influenced by the oxidation and reduction treatment. This implies the inter-grain ordering is affected by the oxygen vacancy despite the stoichiometric composition. In the present work, we performed linear and non-linear resistivity measurements for the ultra-fine Y124 ceramics with different sintered time and investigated the oxidation and reduction effects of the successive superconducting transition.

2. Experimental

Ultra-fine Y124 ceramics were prepared by the citrate pyrolysis precursor method which can make homogeneous grains of submicron size. [4] The precursor was calcined at 778 ^{o}C for 120 h, and sintered at 780 ^{o}C for 12.5 to 200 h.

In the present work, for the annealing treatment, the samples were oxidized at 500 ^{o}C for 24 h flowing 0.2 l/min oxygen gas. After electrical resistivity measurements, each sample was vacuum-heated at 450 ^{o}C for 24 h as a reduction treatment. Although the attained oxygen degree was estimated by measuring weight loss of the sample, obvious mass change was not observed.

The electrical resistivity measurements were performed by 4-probe method applying AC current of 23.0 Hz. Linear resistivity and non-linear resistivity are defined as the coefficients of the first and the third power term of the voltage response, respectively.

3. Results and Discussion

We performed scanning electron microscope (SEM) observations and X-ray diffraction (XRD) analysis for the samples with different sintered time to estimate the grain size. Figure 1 shows SEM images and XRD patterns for the samples sintered for 25 h and 200 h. SEM images show a weak sintered structure with submicron scale grains. The sintering process fuses and joins the adjacent grains. The estimated grain size was less than 0.8 μm for 25 h sintered sample and 1.2 μm for 200 h sintered one. The XRD peaks tend to sharpen with increasing sintered time, which also reflects the microscopic crystal growth.

Figure 2 shows the temperature dependence of the linear resistivity $\rho(T)$ for oxidized and reduced Y124 ceramics. The onset of the superconducting transition temperature T_C^{onset} is indicated in each figure. T_C^{onset} was about 81 K for all samples, regardless of whether the samples were oxidized or reduced. This suggests the intra-grain ordering is independent of the reduction treatment.

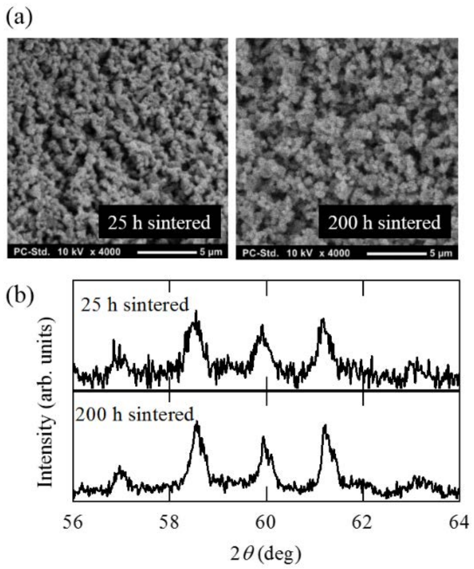

Figure 1. (a) SEM images and (b) XRD patterns for the Y124 ultra-fine ceramics sintered for 25 h and 200 h. To compare the peak width, XRD patterns are expanded.

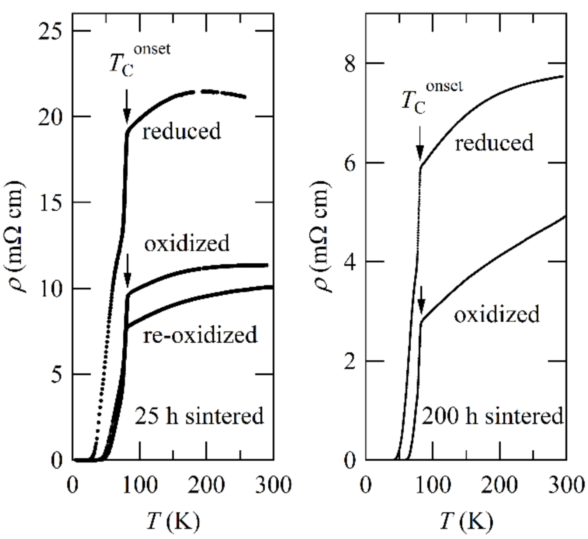

Figure 2. Temperature dependence of the linear resistivity up to the room temperature. The sintered time is shown in each view.

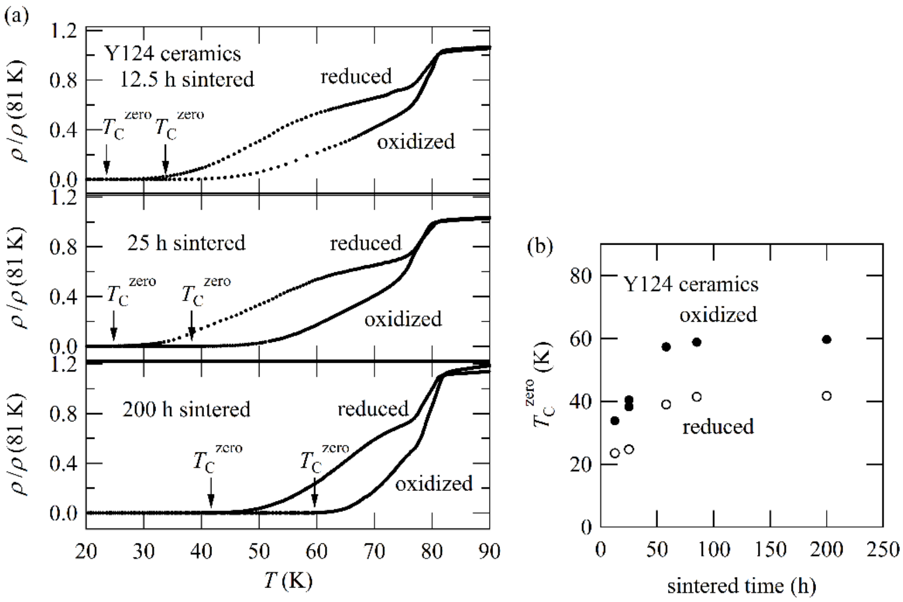

Figure 3. (a) Expanded views of the linear resistivity near the superconducting transition temperature. The sintered time is shown in each view. T_C^{zero} indicates the temperature of zero resistivity. (b) Sintered time dependence of T_C^{zero}.

$\rho(T)$ for the oxidized sample shows T-linear behaviour above T_C^{onset}. The reduced sample also shows metallic behaviour but the $\rho(T)$ curve is convex, which indicates a small part of the sample changes to semiconductive. This reduction effect is reversible; the $\rho(T)$ curve returns to the original shape by re-oxidizing treatment.

Figure 3 (a) shows the expanded views of the temperature dependence of the linear resistivity for Y124 ceramics with different sintered time near the superconducting transition temperature. In these figures, the linear resistivity is normalized to the value at 81 K and the temperature of zero resistivity T_C^{zero} is indicated. Focusing on the sintered time, the 12.5 h sintered sample shows the most gradual transition. This tendency is remarkable in the lower superconducting transition and T_C^{zero} decreases by more than 25 K. As mentioned above, the sintering process makes the grain size bigger. Putting these results together, the lower transition seems to be affected by the total surface area of the grains, which is in agreement with the previous report that T_C^{zero} is attributed to the inter-grain ordering among the superconducting grains by Josephson-coupling through the boundary. [1, 3]

Interestingly, T_C^{zero} shows a further decrease by the reduction treatment for every sintering condition specimens. This nature suggests the oxygen vacancy is induced on the grain surface area which governs the inter-grain couplings. T_C^{zero} recovered to the initial temperature by the re-oxidizing treatment, as is the case with the metallic behaviour above T_C^{onset}. T_C^{zero} is shown against the sintered time in Figure 3 (b). T_C^{zero} increases with increasing the sintered time at first, but it shows little change above about 85 h. This suggests each grain reaches mature size.

We performed non-linear resistivity measurements to investigate the transition process from intra-grain to inter-grain orderings. The third harmonic voltage response $V_{3\omega}$ shows a remarkable negative peak at around T_{peak}. Figure 4 (a) shows the temperature dependence of $V_{3\omega}$ which is normalized to the value at T_{peak}. We estimated a full width at half maximum (FWHM) as shown in Figure 4 (b).

The peak width reflects the inter-grain ordering process. FWHM decreases with increasing the sintered time, but it shows little change above 85 h, as is the case with T_C^{zero}. Because the inter-grain ordering is suggestive of the chiral glass ordering which is characteristic of the ceramic system composed of submicron grains, the crystal growth would suppress FWHM.

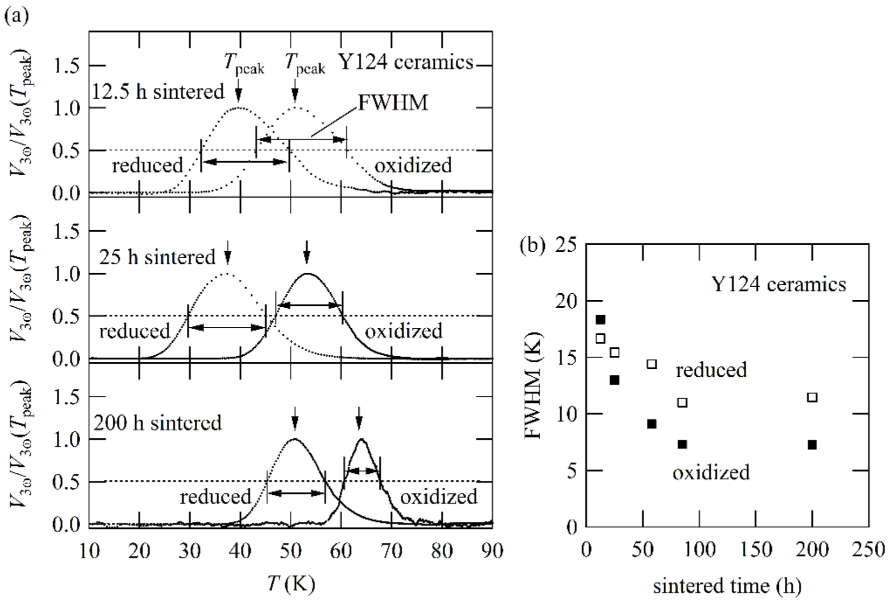

Figure 4. (a) Temperature dependence of the non-linear resistivity. The sintered time is shown in each view. T_{peak} indicates the peak temperature of $V_{3\omega}$. (b) Sitered time dependence of FWHM.

By the reduction treatment, FWHM tends to increase but that for the 12.5 h sintered sample shows no change within the experimental accuracy. This indicates the grain size has a stronger influence on the inter-grain ordering than the reduction effect.

Our experimental results may suggest the ultra-fine Y124 ceramics have peculiar surface on which oxygen vacancy can be induced. Because the inter-grain ordering among the superconducting grains is caused by Josephson-coupling on the grain surface, the oxidation and reduction effects could be observed.

Recently, the superconducting behaviour was found in reduction-treated $PrBa_2Cu_4O_8$ / $PrBa_2Cu_3O_{7-\delta}$ ceramics mixtures, which is considered to be caused by the inter-grain charge transfer effect from CuO single chain to CuO double chain. [5] The similar charge transfer might be induced by the reduction effect on the surface of the submicron grains.

4. Conclusions

We performed linear and non-linear electrical resistivity measurements for the ceramic material composed of Y124 submicron grains and investigated the oxidation and reduction effects of the successive superconducting transition. As the submicron grains increase in size by the sintering process, the inter-grain ordering was suppressed. The reduction effect was observed for the inter-grain ordering, although Y124 is stoichiometric. This suggests that the oxygen vacancy was induced on the grain surface.

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