ISS2011

Optimization of annealing processes on superconductivity of FeSr₂YCu₂O₆₊δ

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Abstract

FeSr₂YCu₂O₆₊δ (Fe1212) shows superconductivity only after proper annealing in N₂ flow, subsequently, annealing in O₂ flow and under high O₂ pressure. In order to optimize each of the annealing temperature for superconductivity, Fe1212 samples were annealed at various temperature in each annealing process. The optimized annealing condition is annealing in N₂ flow at 790 ℃, annealing in O₂ flow and under high O₂ pressure at 270 ℃. The resistance began to decrease at 64 K and dropped to zero at 40 K. Superconductivity of Fe1212 was affected by temperature of N₂ annealing process rather than that of O₂ annealing. The N₂ annealing affects the offset superconducting transition temperature rather than the onset superconducting transition temperature. This implies the inter-grain superconductivity in ceramic Fe1212 is affected by N₂ annealing temperature.

Keywords: FeSr₂YCu₂O₆₊δ; Fe1212; magnetic superconductor

1. Introduction

Since the Fe ion in Cu(2) site suppresses the superconductivity[1,2], FeSr₂YCu₂O₆₊δ (Fe1212) shows superconductivity only after proper annealing processes. Annealing processes in N₂ flow, in O₂ flow and under high O₂ pressure are indispensable for the superconductivity of Fe1212. The Reitveld refinement of the neutron diffraction pattern revealed that the crystal system is tetragonal and 25% of Fe ion distributes to the Cu(2) site before the annealing processes. The oxygen content calculated from the occupation factor of the oxygen is $6 + \delta = 7.36[3]$. The $^{57}$Fe Mössbauer study[4] and the neutron diffraction study[3] revealed that the annealing in N₂ flow suppresses Fe ion distribution to the Cu(2) site. After N₂ annealing, the structure was distorted to orthorhomic and the oxygen content, $6 + \delta$, was decreased to 6.9. The orthorhombic - tetragonal structure change was observed at $6 + \delta = 7.10[5]$.

After N₂ annealing, annealings in O₂ flow and under high O₂ pressure supply the carriers to the CuO₂ planes. After these annealing, less than 10 % of Fe ion distributes to the Cu(2) site[3,6]. The superconducting transition temperature of the sample annealed in the annealing in N₂ flow at 800 ℃, in O₂ and under high O₂ pressure at 350 ℃ is 56 K in the resistivity measurement[4].
Curie-Weiss paramagnetism was observed above superconducting transition temperature. An anomaly was observed at 20 K in the temperature dependence of the magnetization[7]. Magnetism of FeSr2YCu2O6+δ was studied[7] since the distribution of Zn ion in Cu(2) site suppresses the superconductivity[2]. Similar anomaly was observed and it corresponds to the magnetic ordering of Fe ion[7]. The magnetism of Fe ion below 20 K seems to be antiferromagnetism because the asymptotic Curie temperature is negative. Since no extra reflection due to the magnetic superstructure was observed in the neutron diffraction study in low temperature, the long range magnetic order in Fe ion in Cu(1) site was not confirmed[8]. The defect and disorder of the oxygen around Fe ion was considered to retard the long range magnetic order.

In each annealing process, the magnetism and superconductivity of Fe1212 depend on the annealing temperature. To study the superconductivity and magnetism of Fe1212 system, the optimization of the annealing processes for superconductivity is necessary. The purpose of this study is to optimize the annealing temperature to study superconductivity of Fe1212 and other related materials.

2. Experiment

Polycrystalline samples of FeSr2YCu2O6+δ were synthesized by the solid state reaction of stoichiometric mixture of Y2O3, SrCO3, CuO and Fe2O3 powders. The mixture was calcined at 850 °C for 24 h in air and was ground and pressed into pellets. The pellets were sintered at 950 °C for 24 h in air.

Firstly, to make clear the effects by N2 annealing temperature, T_{N2}, the as-synthesized samples were annealed for 24 h in N2 flow at T_{N2} = 730, 750, 770, 790, 810 and 830 °C, subsequently for 24 h in O2 flow and under high O2 pressure at T_{O2} = 350 °C for 24 h. The annealing processes are summarized in Fig. 1. We call the samples after each process the N2 annealed, O2 annealed, and oxidized samples. Secondly, according to the results of N2 annealing process, the as-synthesized samples were annealed for 24 h in N2 flow at optimized temperature 790 °C and, as following processes, the samples were annealed in O2 flow and under high O2 pressure (20 MPa) at T_{O2} = 240, 270, 310, 350, 390, 430 and 470 °C for 24 h in each annealing.

The crystal structure was characterized by x-ray powder diffraction using CuKα radiation. Susceptibility measurement was performed using a SQUID magnetometer (MPMS-XL, Quantum Design) in the magnetic field of 10 Oe. Resistivity was measured by a conventional four-probe method. Oxygen content was deduced based on oxygen content of as-synthesized sample as 7.36[3] by measurement of difference of the sample mass after each annealing.
3. Results and Discussion

The crystal structures were distorted to orthorhombic structure after N₂ annealing except the N₂ annealed sample at $T_{N_2} = 830$ °C. In the N₂ annealed samples annealed at below 810 °C, obvious differences of the lattice parameters were not observed. Oxygen content of N₂ annealed samples were $6 + \delta = 6.97 \sim 7.04$. This indicates that the oxygen content, $6 + \delta$, was not affected by the N₂ annealing temperature.

Fig. 2 shows the temperature dependence of the magnetization under the magnetic field of 10 Oe. The oxidized samples annealed below $T_{N_2} = 810$ °C showed diamagnetism below $T_{c}^{MT} \sim 60$ K due to the superconductivity, where $T_{c}^{MT}$ is the onset temperature of superconducting transition. The diamagnetism observed at the oxidized sample annealed at $T_{N_2} = 830$ °C was weaker than that observed in the oxidized samples annealed at $T_{N_2} = 730 \sim 810$ °C. The crystal system of the N₂ annealed sample at $T_{N_2} = 830$ °C was tetragonal. Without crystal structural change to orthorhombic after N₂ annealing, diamagnetism of the oxidized sample was weak. This structural change to orthorhombic from tetragonal seemed to be related to the suppression of the Fe ion to Cu(2) site[3]. $T_{c}^{MT}$ were decreased with increasing N₂ annealing temperature.

The anomalies were observed at around 10 K. This indicates some magnetic order of Fe ion[7]. The anomalies were not affected by N₂ annealing temperature.

The temperature dependence of the resistance was shown in Fig. 3. The resistance was normalized by the values at 290 K. Semiconducting like temperature dependence of the resistivity was observed above 60 K and the resistance began to decrease in all oxidized samples below around 60 K. $T_{c}^{onset}$ is the temperature where the resistivity begin to decrease and $T_{c}^{offset}$ is the temperature where resistivity reached to zero. Zero resistivity was observed below $T_{c}^{offset} = 15 \sim 40$ K where the oxidized sample annealed at $T_{N_2} = 750 \sim 810$ °C.

The N₂ annealing temperature dependence of the transition temperatures, $T_{c}^{onset}$, $T_{c}^{offset}$ and $T_{c}^{MT}$, were shown in Fig. 4. The maximum $T_{c}^{MT}$ was observed at 62 K in the oxidized sample with $T_{N_2} = 750$ °C in magnetization measurement. $T_{N_2}$ dependence of $T_{c}^{onset}$ were similar to that of $T_{c}^{MT}$ in magnetization measurement. In contrast, a narrow peak was observed in the dependence of $T_{c}^{offset}$. The optimized annealing condition is annealing in N₂ flow at 790 °C. Generally, the inter-grain superconductivity affects $T_{c}^{offset}$, while the intra-grain superconductivity affects $T_{c}^{MT}$ and $T_{c}^{onset}$. This difference of these transition temperature indicates that inter-grain superconductivity in ceramic Fe1212 was affected by $T_{N_2}$. For optimizing the annealing temperature, the resistivity measurement was appropriate to superconductivity of Fe1212 compared with the magnetization measurement.

![Fig. 2. Temperature dependence of the magnetization for FeSr₂YCu₂O₆₊₆ under the magnetic field of 10 Oe. The arrows indicate the anomalies due to the some magnetic order.](image)

![Fig. 3. Temperature dependence of the resistances for FeSr₂YCu₂O₆₊₆. The values of resistivity are normalized with the resistances at 290 K. The arrows indicate the $T_{c}^{onset}$.](image)
Fig. 5 shows the relation between the transition temperatures, \( T_{c_{\text{onset}}} \), \( T_{c_{\text{offset}}} \) and \( T_{c_{\text{MT}}} \), and the annealing temperature, \( T_{O2} \), in O2 flow and under high O2 pressure. Oxidized samples annealed at above \( T_{O2} = 270 \, ^\circ\text{C} \) showed zero resistivity. The superconducting transition temperature of Fe1212 was affected by annealing temperature, \( T_{O2} \), above 270 \, ^\circ\text{C} \) in O2 flow and under high O2 pressure. Both intra-grain and inter-grain superconductivity were affected similarly by \( T_{O2} \). The effect of O2 annealing is smaller than that of N2 annealing. The optimized annealing condition is annealing in O2 and high O2 pressure at 270 \, ^\circ\text{C} \). Oxygen content of these samples were 6 + \( \delta = 7.55 \sim 7.67 \). As oxygen content, 6 + \( \delta \), of oxidized samples were little affected by \( T_{O2} \), the annealing at too high \( T_{O2} \) seems to deteriorate the distribution of Fe ion in Cu(1) site.

![Fig. 4. Relation between the transition temperatures, \( T_{c_{\text{onset}}} \), \( T_{c_{\text{offset}}} \), \( T_{c_{\text{MT}}} \) for FeSr2YCu2O6+\( \delta \) and N2 annealing, the samples are annealed in O2 flow and under high O2 pressure at 350 \, ^\circ\text{C} \).]

![Fig. 5. Relation between the transition temperatures, \( T_{c_{\text{onset}}} \), \( T_{c_{\text{offset}}} \), \( T_{c_{\text{MT}}} \) for FeSr2YCu2O6+\( \delta \) and annealing temperature, \( T_{O2} \), in O2 flow and under high O2 pressure.]

4. Conclusion

To study the magnetism and superconductivity of Fe1212, the annealing conditions in N2 flow, in O2 flow and under high O2 pressure were optimized. The optimized annealing temperature are 790 \, ^\circ\text{C} \) in N2 flow and 270 \, ^\circ\text{C} \) in O2 flow and under high O2 pressure. The highest \( T_{c} \) of Fe1212 in this study was \( T_{c_{\text{onset}}} = 64 \, ^\circ\text{K} \) and at \( T_{c_{\text{offset}}} = 40 \, ^\circ\text{K} \) in the resistivity measurement. Superconductivity of Fe1212 was affected by temperature of N2 annealing process rather than O2 annealing, while oxygen content, 6 + \( \delta \), was not affected by the N2 annealing temperature. The inter-grain superconductivity in ceramic Fe1212 seems to be affected by N2 annealing temperature, \( T_{N2} \).

References