Relationship between Carrier Concentration and Superconducting Transition Temperature in Bi-Sr-Ca-Cu-O Superconductor

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요 약. 초산염(acetate)을 출발원료로 하여 $Bi_2Sr_2Ca_2Cu_3O_y$계 단일상 고온초전도체를 합성하려 하였으며 그 초전도상의 형성과정을 초전도전이온도 T_c 및 전하나르게 농도와의 상관관계로부터 설명하고자 하였다. 초전도전이온도 T_c는 전기저항밀도 및 자화율을 측정하여 결정하였다. 시료로는 상기의 초전도체 출발조성물의 하소분말에 대해 850℃, 860°, 그리고 870℃에서 40시간 동안 공기 중 열처리한 것을 이용하였다. 전하나르게농도는 홀계수를 측정하여 구하였다. 열처리과정 중의 초전도체 형성과정을 세라믹벌크내에 형성된 초전도체의 양 및 전하나르게농도 분포의 상관관계로부터 설명하였다.

ABSTRACT. $Bi_2Sr_2Ca_2Cu_3O_y$-based superconductor phases were synthesized by the wet process using acetate precursors. Superconducting transition temperature (T_c) was determined from both measurements of electrical resistivity and magnetic susceptibility for the samples which were sintered at the temperatures of 850℃, 860℃, and 870℃ for 40 hours, respectively. The values of carrier concentration from Hall measurements were compared with T_c data as a function of the sintering temperature. The formation mechanism of the superconducting phase was tentatively discussed on a basis of the distribution profile concept of the carrier concentration and the amount of superconducting phases in a ceramic bulk. This explanation may be supported by the experimental results of correlation between the relative amount of superconducting phases and the difference of T_c values between superconducting onset temperature and cutoff temperature at each sintering temperature.

Key Words : Bi-Sr-Ca-Cu-O Superconductor, Superconducting transition, formation mechamism.

1. Introduction

Since the first reporting on the high T_c superconductor by Bednorz and Muller[1], there have been lots of studies[2,3]on the superconducting mechanism of La_2CuO_4 system including YBCO and Bi(Tl)-Sr-Ca-Cu-O which have been found immediately. Among the methods for explaining the conduction mechanism of high T_c superconductor one of the most probable concept is the correlation of the superconducting transition temperature, T_c, with the electron/hole concentration. Therefore many authors have reported[4~8] the Hall coefficient as an indicator of the carrier concentration in relation with T_c for the purpose of explaining the conduction mechanism in high Tc superconductor.

It has been well known that synthesis of a exclusively single phase in Bi-Sr-Ca-Cu-O-based superconductor system is very difficult[9, 10]. Even though there has been much effort to prepare the bulk

superconductor with a single 2223 phase, the synthesis of a purely high T_c phase has been little reported on the sintered bodies[11]. Moreover, the reason is not yet clearly understood until now.

In this study the authors have investigated the correlation between carrier concentration from Hall coefficient measurement and T_c for the sintered bodies of Bi-Sr-Ca-Cu-O system superconductor and made an effort to explain the formation mechanism of a superconducting phase.

2. Experimental Procedure

The metal acetates were selected as highly reactive precursors both to attain the homogeneity in mixing and calcination and to make it possible to obtain a single phase of high T_c superconductor. Bismuth acetate(Kanto Chemical, special grade), strontium acetate (Wako Purechemical, special grade), calcium acetate (Wako Purechemical, special grade) and copper acetate(Wako Purechemical, special grade) were verified as above 99.9% purity.

Appropriate amounts of each reagent were weighed and then dissolved in deionized water to give a homogeneous solution of metal acetates. The solution was moderately evaporated and dried in a beaker on the hot stirrer. The homogeneous mixture of metal acetates was placed in an alumina crucible and then heated to the decomposition temperatures between 150°C and 300°C. After decomposition, the obtained black fine powders were ground in an agate mortar and calcined in muffle furnace at 800°C for 24 hours. The calcined powders were pelletized by dry press and sintered in air at 850°C~870°C for 40 hours and slowly cooled in furnace. The composition for all test samples were selected as 2:2:2:3 for Bi:Sr:Ca:Cu.

The crystallographic phases formed during sintering were determined by X-ray diffractometer (JEOL). Hall effects at room temperature were measured by RESITEST 8200 (Toyo Technica Co. Ltd.,) and silver paste was applied as an electrode material. Hall effect measurement for thin film as a standard four probe

DC measurement was adopted on the rectangularly sliced flat thin samples of the sintered bodies in a magnetic field of 1.5 T at room temperature. Superconducting transition temperature, T_c was determined by both electrical resistivity and magnetic susceptibility measurement. The electrical resistivity measurement was performed using DC 4 point probe method in a helium cryostat and the magnetic susceptibility was measured with a QUANTUM DESIGN (MPMS SQUID) susceptometer to characterize the exact T_c value and the relative amount of each superconducting phase. The Meissner effect was measured in a field of 2mT during warming up after cooling.

3. Results and Discussion

Decomposed acetate mixtures were in an amorphous form, but after sintering and annealing process it resulted in the well developed platelike crystals of superconductor phase. A significant amount of high Tc phase could not be detected in all samples by XRD as shown in *Fig.* 1, but the resistivity drop and Meissner effect were observed at 108 K for all tested samples.

Fig. 2 shows the temperature dependence of the resistivity for $Bi_2Sr_2Ca_2Cu_3O_y$ samples which were sintered at the different temperatures of 850°C, 860°C, and 870 °C for 40 hours as indicated. The specific resistivity at temperature above $T_{c, off}$ increases drastically, whereas below that no significant difference in resistivity is observed. Among the above samples the increase of firing temperature leads to the lowering of resistivity and the increase of T_c value.

Fig. 3 represents the magnetic susceptibility measured by SQUID magnetometer for the samples in *Fig.* 2. $T_{c, on}$ was decided by the data analysis method of Koike et. al[5] in ρ vs T plot and X vs T plot. The midpoint of the transition curve in ρ vs T plot was selected as $T_{c, on}$ and this onset temperature of superconduction was well identified with the defined value in X vs T plot where the extrapolated line of the steepest part as shown in *Fig.* 3 reaches the normal
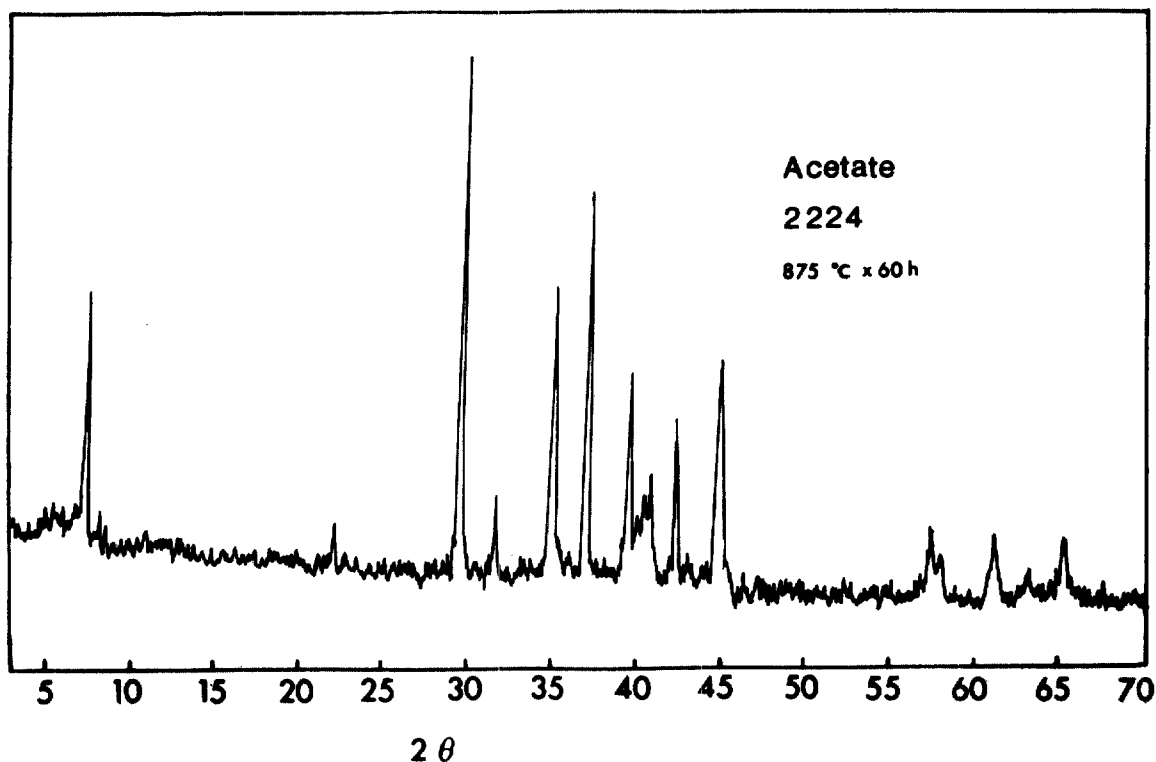
Fig. 1. X-ray peaks for the $Bi_2Sr_2Ca_2Cu_3O_y$ samples which sintered at 875°C for 60 hours in air. There exists only a slight 2223 phase.

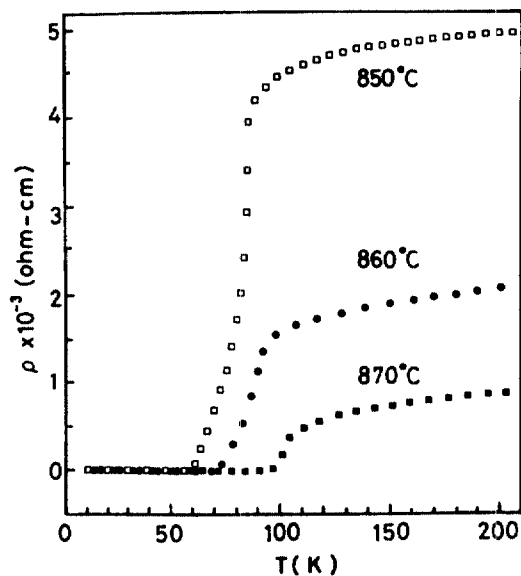

Fig. 2. Electrical resistivity with temperature for the $Bi_2Sr_2Ca_2Cu_3O_y$ samples which sintered at indicated temperatures for 40 hours in air.
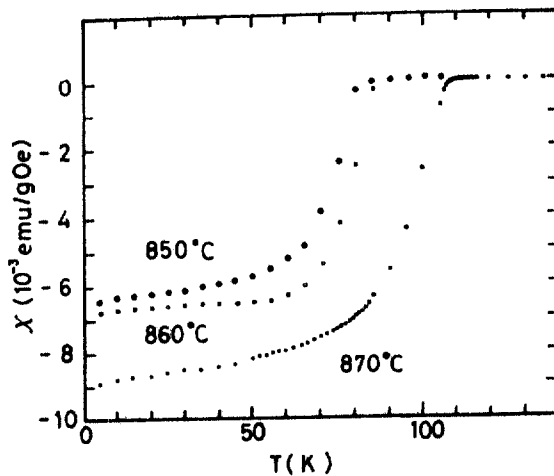

Fig. 3. The magnetic susceptibility with temperature for the samples of Fig. 2. The susceptibility values were determined by the SQUID susceptometer and these values were normalized.

state value of χ. These experimental results show the
T_c, on and T_c, off explicitly and the relative amount of
the superconducting phase among the tested samples
can be estimated from the level of the normalized sus-
ceptibility values. From the above results, it is noted
that T_c, on of and T_c, off each sample increase with the
increase of firing temperature. As a result the gap of
superconducting temperature T_c between T_c, on and T_c,
off gradually decreases with the increase of sintering
temperature in the tested temperature region. The
normalized values of magnetic susceptibility roughly
increase with the increase of firing temperature as
shown in *Fig.* 4. The increase of firing temperature
leads to the improvement of T_c level, the decrease of T_c
gap, and the continuous increase of the amounts of the
high T_c superconducting phase in the bulk.

In starting materials from the calcined powder, it
may be postulated that there are mixtures of several
kinds of phases such as nonsuperconducting phase,
lower T_c phase, middle T_c phase, and/or higher T_c
phase, etc. From this viewpoint, it is interesting to in-
vestigate the behavior of the carrier concentration and
the firing temperature for the purposes of understand-
ing the mechanism of the increase of T_c level and the
formation of superconducting phase in the phase
mixtures mentioned above. *Fig.* 4 shows the relation-
ship between the values of T_c, on and T_c, off and the
relative amount of superconducting phase estimated
from χ value in *Fig.* 3. Besides the variation of the hole
concentraion, $1/R_H e$ with temperature at room tem-
perature, estimated from Hall coefficient R_H are shown
together. The carrier concentration in the bulk
monotonically increases with the increase of firing tem-
perature in the tested temperature range as shown in
Fig. 4, which is due to the decrease of electrical resis-
tivity with the increase of firing temperature. Essen-
tially Bi-Sr-Ca-Cu-O-based superconductor is a p-type
conductor of hole carrier from Hall effect measurement
and so the' increase in the hole carrier concentation
must lead to the lowering of electrical resistivity.

From the forgoing discussion we can draw such a
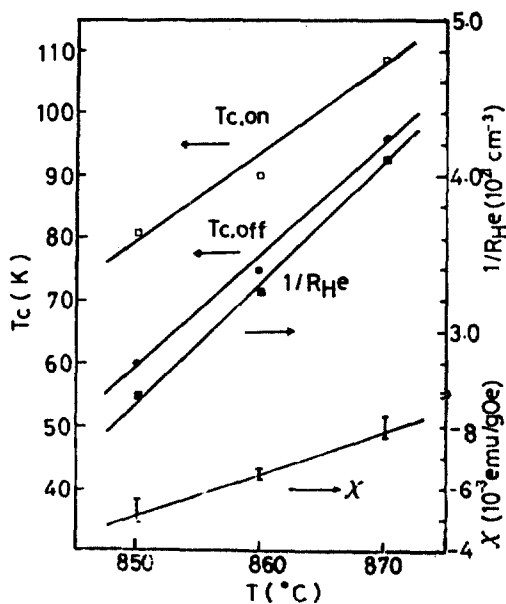structural image that several kinds of superconducting

Fig. 4. The correlation between T_c, hole concentration
$1/R_H e$ at room temperature estimated from Hall coefficient
R_H and the relative amount of superconducting phases in
the $Bi_2Sr_2Ca_2Cu_3O_y$ which are sintered at temperatures of
850°C, 860°C, and 870°C for 40 hours in air. The relative
amount of superconducting phases was estimated from the
normalized values of magnetic susceptibility of *Fig.* 3.

phases and nonsuperconducting phases are mixed in a
bulk and there is a local composition fluctuation
within the individual phases of the starting calcined
powders. It can be supposed that the phase with lower
T_c value has the lower level of carrier concentration,
because the T_c level of a superconducting phase is well
proportional to the carrier concentration. The amount
of a superconducting phase or a nonsuperconducting
phase in the bulk may be distributed over the carrier
concentration values with some range. It seems that the
bulk phase does not take a single value of carrier con-
centration in the sintered body of high T_c
superconductor because of the inevitably existing
chemical inhomogeneity. We can consider the corre-
lation between the carrier concentration distribution
and the relative amount of superconducting phases
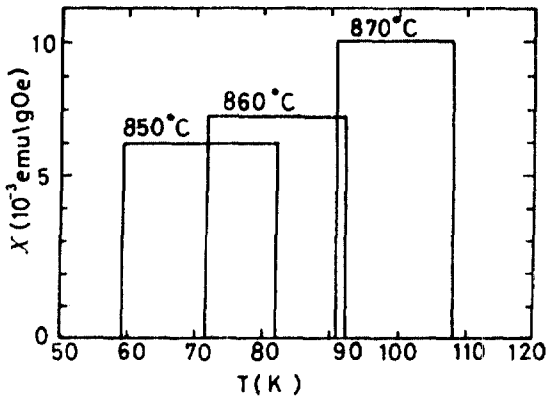and/or nonsuperconducting phases in a bulk. When

Fig. 5. The normalized value of magnetic susceptibility
with T_c, on and T_c, off for the $Bi_2Sr_2Ca_2Cu_3O_y$ samples which
were sintered at the temperatures of 850°C, 860°C, and
870°C for 40 hours in air, respectively. The relatively
normalized values of χ were roughly estimated from *Fig.* 3.
and schematically plotted against the distribution of T_c
values between T_c, on and T_c, off to express the disitribution
profile of the amount and T_c values of superconducting
phases.

this starting material is fired at sintering temperature
the superconducting phases in the bulk will be formed
and the carrier concentration of each phase will be
distributed over some range according to the firing
schedule. The distribution profile and the amount of
the carrier concentration may be fluctuated and
overlapped among the various phases in the bulk dur-
ing the firing process. This hypothetically suggested
distributional behavior of phases and their carrier con-
centration in a sintered body may be caused by the
compositional and/or chemical variation which is inevi-
tably introduced in the proparation process. If we use
the highly reactive precursor such as e.g. acetates in the
preparation, the inhomogeneity may be considerably
diminished and so the distribution profile become
sharper. In reality the above explanation will be
supported by the relationship of χ vs T_c, on and T_c, off
plot as shown in *Fig.* 5. In this figure the normalized
value of magnetic susceptibility estimated from *Fig.* 3
are plotted against the distribution of T_c values be-

tween T_c, on and T_c, off to express the distribution pro-
file of the amounts and T_c values of superconducting
phases. So the amounts of the superconducting phases
are distributed over the some range of T_c values.
Therefore the successively rapid drop in the transition
region in ρ - T or χ - T curve is observed and it may
be accounted for the existence of various
superconducting phases wih their T_c values in a bulk.
From the above discussion it can be said that there
may be lots of phases with a different carrier concen-
tration and T_c value in a superconductor bulk. Accord-
ingly, it is concluded that to get the single 2223 phase
requires preparation of a homogeneous powder, ex-
tremely accurate furnace temperature control and very
long annealing.

4. Conclusion

The formation mechanism of superconducting phases
in $Bi_2Sr_2Ca_2Cu_3O_y$ bulk can be discussed on a basis of
the correlation of carrier concentration, $1/R_{He}$ and
superconducting transition temperature, T_c. It may be
considered that there are distribution profiles between
the carrier concentration and the amount of
superconducting phases with their T_c values in a bulk
and the distribution will be fluctuated and overlapped
among the various phases during the sintering process.
This-like distribution profile may be accounted for the
difficulty of the synthesis of a singly pure high T_c phase
in Bi-Sr-Ca-Cu-O superconductor system and so to ob-
tain the single 2223 phase requires accurate furnace
temperature control and very long annealing.

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