Y_2O_3-BaO-CuO 3성분계 상도에서의 초전도 영역에 관한 연구

Study on the Superconducting Region in the Ternary Phase Diagram for the Y_2O_3-BaO-CuO System

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요 약

22종류의 Y-Ba-Cu-O계 세라믹스의 초전도성을 조사하기 위하여 x-선 회절무늬, 전기 / 저항 및 적외선 투과도를 측정하였다. 또한 시료의 제조 조건에 따른 영향도 조사하였다. 측정결과 3성분계 상도에서 넓은 영역에 걸쳐 초전도성이 나타났으며, 특히 상도의 중앙 부근의 조성을 갖는 시료들은 실온에서 전기 저항값이 작고 90 K 이상에서 초전도 전이가 일어남을 알 수 있었다.

Abstract

In order to examine the superconductivity of various Y-Ba-Cu-oxide ceramics, we fabricated twenty-two samples. We measured X-ray diffraction pattern, electrical resistance and IR transmittance.

The effect of the preparation conditions was also examined. With the best preparation conditions, the superconductivity was found in very wide region of the ternary phase diagram. Especially, samples in the central region of the ternary phase diagram show the superconducting onset temperatures around 90K, and very low resistance values at room temperature.

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INTRODUCTION

Since the high T_c superconductor was discovered in lanthanum-barium-copper-oxide (LBCO) system,[1] the various efforts have been made to have better situations, i.e. higher T_c, larger critical current and so on.[2] The recent research by Chu et al. has raised T_c as high as 90K in yttrium-barium-copper-oxide (YBCO) system.[2,3] The new subject of oxide superconductor appears to be very important both in viewpoint of material science and in viewpoint of pure physics.

In spite of a number of theories and experiments to explain or to understand the physics of the high T_c superconductors,[4] our knowledge about the nature or the origin of their superconductivity is extremely limited.

Among the high T_c superconducting materials, the YBCO system has been investigated frequently because of its high superconducting temperature.[5] The synthesizing process of the YBCO system has been studied proviously, but the systematic and comprehensive investigation is necessary.

In this study, we fabricated a number of YBCO compositions, and examined the reproducibility and stability of YBCO ceramics. We reexamined the ternary phase diagram for the Y_2O_3-BaO-CuO system,[5] tried to find the best preparation conditions and investigate the superconductivity for many compositions.

SAMPLE PREPARATIONS

We fabricated YBCO samples by mixing individual raw materials of Y_2O_3, $BaCO_3$ and CuO directly.

Fig. 1 shows the ternary phase diagram for the Y_2O_3-BaO-CuO system. We fabricated 22 samples assigned by A, B,..., V from raw materials of 99.99% purity. Three different

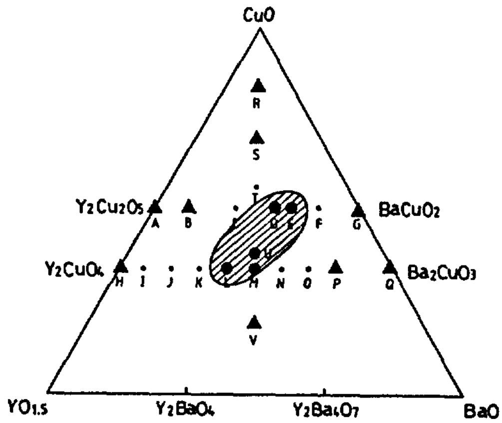


Fig 1. Ternary phase diagram of Y_2O_3-$BaCO_3$-CuO system.

Each point corresponds to the composition for which experiments were performed. Solid triangle, small dot and large dot stand for nonsuperconductors, superconductors with worse properties and superconductors with better properties, respectively (See the text.).

groups (Ⅰ, Ⅱ and Ⅲ) are shown in the phase diagram. Group Ⅰ consisting of samples A to G is chosen, because the general molecular formula is ABO_y-type, i.e. typical perovskite-type in crystal structure. And Chu et al. found the first 90K high T_c superconductor for $Y_1Ba_2Cu_3O_y$ corresponding to sample E in our phase diagram[3]. Group Ⅱ (samples H～Q) is chosen because the samples in this group are likely to be K_2NiF_4-type which is found to be a superconductor in $(La_{1-x}Ba_x)_2CuO_4$ system. In addition to the two parallel lines, a perpendicular line, group Ⅲ, is chosen in order to examine superconductivity with respect to the amount of Cu-ion.

After mixed, calcined and pulverized a few times, the products were cold-pressed in 1 cm diameter with the pressure of 1 ton / cm². Finally our ceramics samples were obtained by sintering in air.

We chose calcining temperature in accordance with partial melting point and sintered all samples below 20℃ to individual partial melting

Table 1. Calcining and sintering comnditions (temperature and time) of the 22 samples in the YBCO system with the best choice. Ratio(x / y / z)represents ratio of Y, Ba and Cu in sample, respectively. Cal. Tem. and Sin. Tem. stand for calcining temperature and sintering temperature, respectively.

SAMPLE	Ratio(x/y/z)	1st Cal.Tem.(time)	2nd Cal.Tem(time)	Sin.Tem.(time)
A	2/0/2	640 (5)	840 (5)	-
B	4/1/5	990 (4)	1,020 (3)	1,020 (2)
C	3/2/5	896 (3)	940 (3½)	940 (2)
D	2/3/5	890 (3)	930 (20)	930 (2)
E	1/2/3	890 (4)	910 (3)	915 (2)
F	1/4/5	840 (1½)	840 (3½)	910 (3)
G	0/1/1	640 (3)	840 (5)	-
H	2/0/1	640 (3)	840 (9)	-
I	9/1/5	990 (4)	1,090 (19)	1,090 (5)
J	8/2/5	1,000 (4)	1,090 (7)	1,210 (4)
K	7/3/5	1,000 (1½)	1,090 (16)	1,210 (4)
L	6/4/5	1,010 (10½)	1,100 (13½)	1,190 (5)
M	1/1/1	940 (2)	950 (2)	990 (2)
N	8/12/10	940 (3)	960 (3)	975 (2)
O	6/15/10	940 (4½)	940 (2)	940 (2)
P	1/3/2	850 (21½)	910	950 (2)
Q	0/2/1	740 (5)	840 (5)	-
R	1/1/13	890 (4)	910 (3)	950 (4)
S	2/2/11	890 (4)	920 (3)	940 (2)
T	1/1/3	890 (4)	920 (3)	940 (2)
U	2/2/3	890 (10½)	890 (5)	940 (2)
V	2/2/1	890 (3)	1,190 (3)	1,240 (2)

point because in general Y-Ba-Cu-Oxide ceramics which are fired near partial melting point are found to have good superconductivity.

Mixing ratio, our best choices of calcined temperatures and times, and a sintered temperature and time are tabulated in Table 1.

The color of samples in Group Ⅰ and Ⅱ changes from dark green to black and the mass density became larger as the ratio of $BaCO_3$ to Y_2O_3 increased.[6] In general, the calcining and sintering temperatures were found to be higher for the yttrium-riched samples in group Ⅱ (i.e. samples I to L), in contrast to the case of group Ⅰ, where these temperatures were nearly equal for all the samples.

EXPERIMENTS AND RESULTS

1. X-ray Diffraction Study

For the comparison, the X-ray diffraction patterns of the raw materials of Y_2O_3, $BaCO_3$ and CuO are shown in Fig. 2-a. The major peaks at $2\theta = 29.17°$ and $48.55°$ for Y_2O_3, at $2\theta = 23.92°$ for $BaCO_3$ and at $2\theta = 35.49°$ and $38.66°$ for CuO have been found.

Fig.2-(b) shows the results of the X-ray diffraction experiment of three samples B, C and E(123) out of 7 in group Ⅰ. The X-ray diffraction patterns of samples D and F are similar to that of sample E. In samples B and C, the contributions of Y_2O_3 and CuO (marked as *) are respectively observed in the X-ray diffraction peaks. However we found the single phase of the typical orthorhombic structure for samples D, E and F.

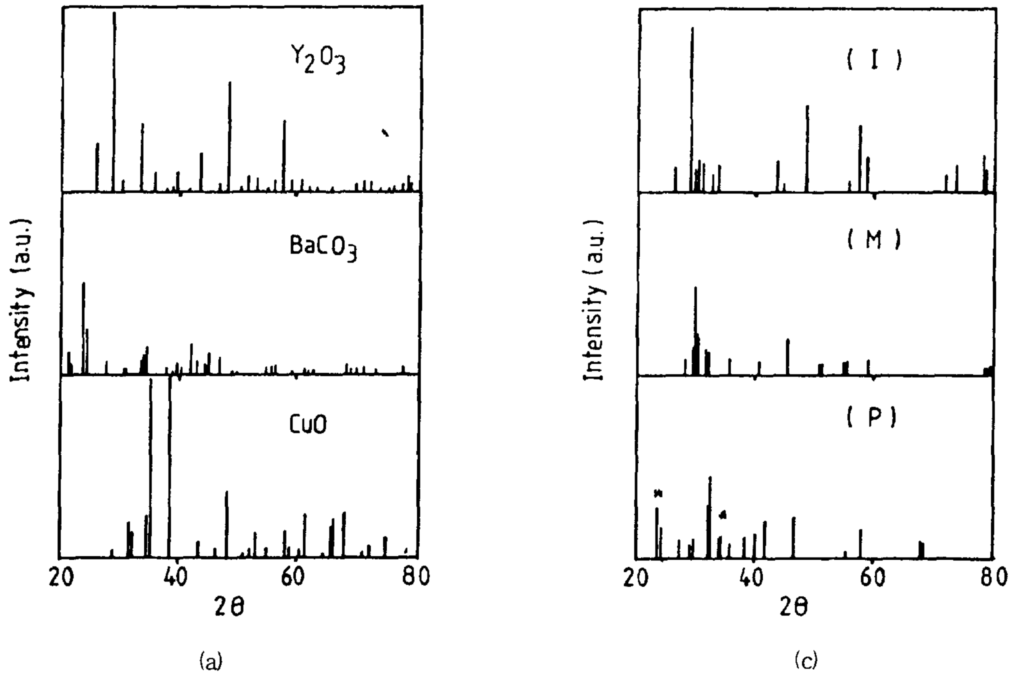
Fig. 2-(c) shows the X-ray diffraction patterms of three samples (I, M and P) out of 10 in group Ⅱ. Samples J, K and L are similar to that of sample Ⅰ. Samples N and O have similar structures to samples M and P, respectively. In sample Ⅰ, the big contributions of Y_2O_3 are observed to be assigned by every single peak. For sample M, we do not have enough X-ray diffration peaks to identify the microscopic details. And in sample P, it is found that the amount of $BaCO_3$(marked as* in Fig.2) is still left a lot.

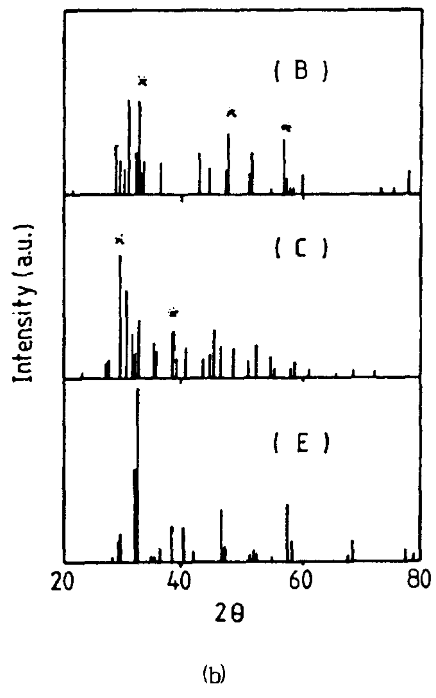
In Fig.2-(d), the X-ray diffraction patterns of samples T and U are shown. For both samples, they appear to be multiphase, especially the extra peaks (maked as *) in addition to the X-ray diffraction peaks of the typical orthorhombic structure for sample U, as observed in sample E.

From the above X-ray results, we can say that the majority of the samples that we prepared in the ternary system are of multidomain except samples D, E and F.

2. Electric Resistance Measurements

The bar-shaped specimens of 1.5×1.5×10㎣ were cut from the pellets and four silver leads were attached to the samples with silver paste. The standard four-probe method was used for electric resistance measurement in the temperature range of 10~300K.





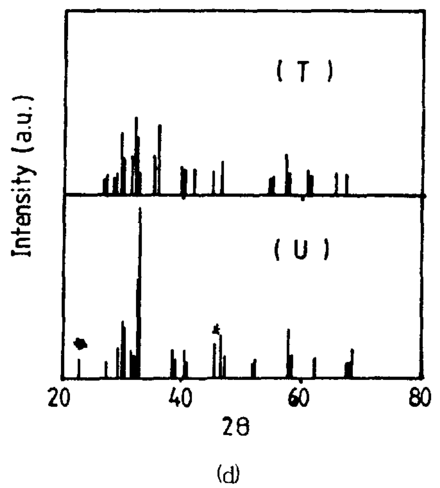


Fig 2. X-ray diffraction patterns of (a) starting materials, (b) group Ⅰ, (c) group Ⅱ and (d) group Ⅲ of YBCO system at room temperature.

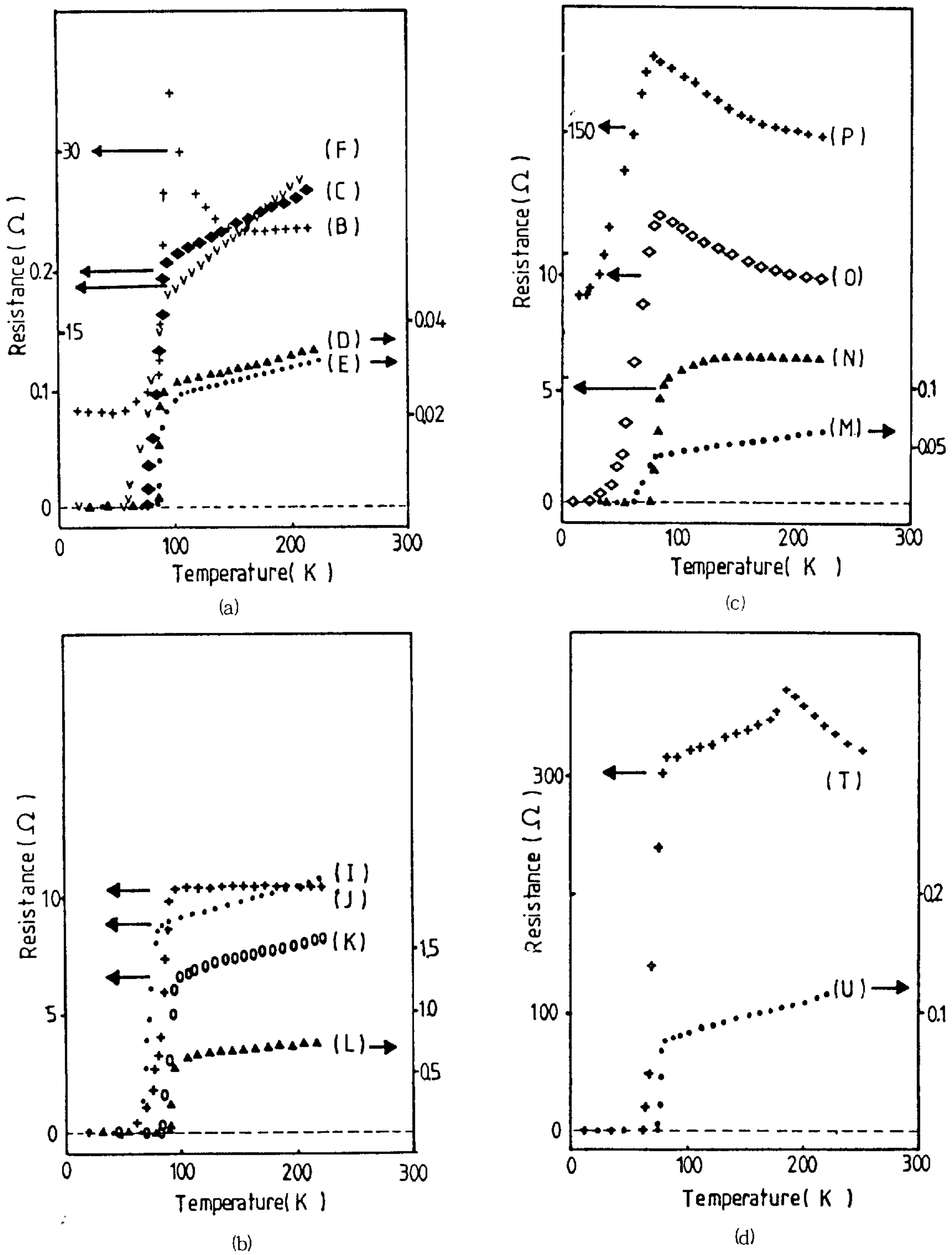


Fig 3. Resistance as a function of temperature of (a) group Ⅰ, (b) and (c) group Ⅱ, and (d) group Ⅲ.

Fig. 3-(a) shows the resistance as function of temperature for group Ⅰ (B~F). Samples A and G which are omitted here, have very high resistance values at room temperature and their values increase with decreasing temperature. Samples C, D, E (123-compound) and F exhibit superconductivity and their transition onset temperature is 96K, 86K, 95K and 84K, respectively. Although the onset temperature of sample C is almost the same as that of sample E. The characteristic of sample B is different from that of the rest of group Ⅰ. While the resistance behavior of samples C~F is metallic in the non-superconducting phase, the resistance value of sample B increases as temperature is lowered from room temperature to 96K where it shows a transition. But, for sample B, we could not observe zero resistance in lower tem-

Table 2. Results of the electrical resistance measurement.
The resistamce values at room temperature and the transition onset temperature are given in the units of Ω and K.
Nonsup. and sup. stand for nonsuperconductor and superconductor, respectively.

SAMPLE	Ratio (x/y/z)	R (290 K)	Ton	Result
A	2/0/2	-	-	Nonsup
B	4/1/5	20	96	Nonsup
C	3/2/5	0.35	96	Nonsup
D	2/3/5	0.04	86	Sup
E	1/2/3	0.03	95	Sup
F	1/4/5	0.31	84	Sup
G	0/1/1	10^5	-	Nonsup
H	2/0/1	-	-	Nonsup
I	9/1/5	12	78	Sup
J	8/2/5	11	83	Sup
K	7/3/5	8.6	96	Sup
L	6/4/5	0.8	96	Sup
M	1/1/1	0.65	82	Sup
N	8/12/10	7.2	86	Sup
O	6/15/10	9.0	80	Sup
P	1/3/2	130	88	Nonsup
Q	0/2/1	10^5	-	Nonsup
R	1/1/13	500	-	Nonsup
S	2/2/11	1,000	-	Nonsup
T	1/1/3	290	80	Sup
U	2/2/3	0.13	76	Sup
V	2/2/1	10^5	-	Nonsup

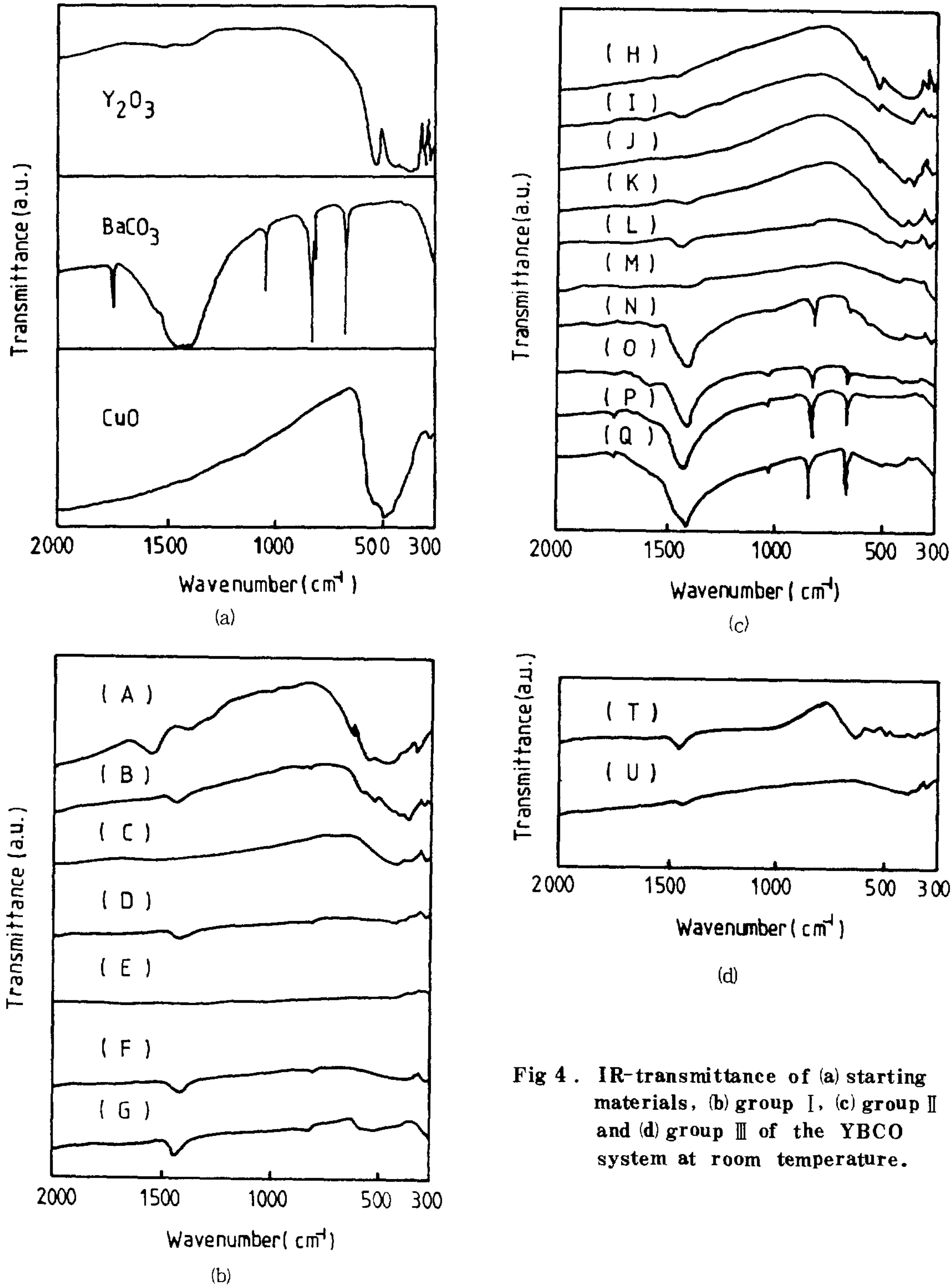


Fig 4. IR-transmittance of (a) starting materials, (b) group Ⅰ, (c) group Ⅱ and (d) group Ⅲ of the YBCO system at room temperature.

perature region.

The resistance-temperature relations of group Ⅱ are shown in Figs. 3-(b) and 3-(c). The binary samples, H and Q, have very high resistance values and show similar behavior to those of group Ⅰ. Also all the ternary samples in this group Ⅱ, exhibit superconductivity except only one sample P. The samples between I and N show metallic behavior and sample O shows semiconductor or insulator behavior in nonsuperconducting phase. The resistamce-temperature relation is very similar to that of sample B in the group Ⅰ. From the measurements for group Ⅲ, it is found that the regions of higher and lower concentration of cu-element (samples R, S and V) are not likely to be superconductor. Fig.3-(d) shows the resistance as function of temperature for sample T and U that show superconductivety. The onset temperature is 80K and 76K, pespectively. For sample T, there is an anomaly in resistance near 200K.

From the above results, we constructed the ternary phase diagram concerning superconductivity. In Fig. 1, the samples with superconductivity are represented by closed circles and dots, and the nonsuperconducting samples by triangles. In contrast to the previous study of the ternary phase diagram by Murakami et al.[5] samples I and J were found to be superconductors in our measurement.

Table 2 summarizes the results of the electrical resistance measurements, including the resistamce values at room temperature and the transition onset temperatures of superconductivity. The nonsuperconducting samples have relatively high resistance values ($\geq 10\Omega$) compared with the superconducting samples ($\sim 0.1\Omega$). Especially the samples in the region connecting samples E to L (shadow region) in Fig. 1 have very small resistamce values at room temperature and show superconductivity near 90K.[7] Furthermore, even though we did not perform the magnetic susceptibility measurement for all the samples, the samples we checked (samples E, L) exhibit the diamagnetism, as we expected.[8]

3. IR Transmittance Experiments

As priliminary data, the IR transmittances of the starting powders, Y_2O_3, $BaCO_3$ and CuO are shown in the region between 300 and 2000 cm^{-1} in Fig. 4-(a).

Fig.4-(b)exhibits the IR spectra of group Ⅰ (samples A~G). The spectra of samples A, B and G appear to be differently from those of the rest. In other words, in the lower wavelength region, there are structures of starting materials, in spectra of samples A, B and G, but not for samples C, D, E and F.

The spectra of group Ⅱ exhibit more interesting behavior, as shown in Fig.4-(c). Although samples I, J, K and L have similar IR spectra to Y_2O_3 and CuO, the superconductivity is found in electric resistance measurement. For Ba-riched side samples (N, O and P), the IR spectra of $BaCO_3$ are strongly observed. From these results, we expect that all the samples (maybe except sample M) have multiphase structure that is divided into two regions, one superconducting and the other nonsuperconducting even in low temperature.

In Fig. 4-(d), the IR of samples T and U are shown. For sample T the spectra shows transmission bump near $800cm^{-1}$ due to CuO, that is believed not to be single phase, but for sample U there are no such structures in spectra.

The data of IR experiment is consistent with those of X-ray diffraction experiment. The samples of the shadow region connecting sample E to L in Fig. 1 that show very high onset temperature and very low resistance value at room temperature, do not have any structure of IR spectra, differently from those of starting materials.

SUMMARIES

In the electric resistance measurements, we construct the ternary phase diagram concerning superconductivity. We especially concentrate on both the ABO_y type and A_2BO_y type. We observe the superconductivity in very wide region for both types. In the central region of the ternary phase diagram (represented by shadow region) the superconducting onset temperature is found to be as high as or higher than 90K and the resistance value is very low at room temperature.

In order to study about structures, the IR spectra and X-ray diffraction patterns are measured. The sample in the central region of group I (samples D, E and F) are believed to be single phasic but almost of all samples in group II are found to be multi-phasic. Despite the multi-phase, seven out of ten samples are observed to be superconductrors in group II.

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