Isolation and Analysis of Micro-regions Having Possibly Higher Tc in Oxide Superconductors*

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酸化物系 超電導體의 高遷移 溫度部分의 抽出과 이의 成分 分析에 관한 硏究

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酸化物 超電導體에 있어서 高遷移 臨界溫度를 갖는 미소영역을 抽出하여 이를 分析 하기위하여 La-Ba-Cu-O 系, Y-Ba-Cu-O 系 및 Bi-Pb-Sr-Ca-Cu-O系의 超電導體를 固相法, 共沈法 및 nitrate solution method로 製造하였다. 제조된 시료들에 대해서 x선회절분석과 저항을 측정하였다. 이들 시료중에서 高遷移溫度를 나타내는 미소부분을 Meissner効果를 이용한 抽出法으로 分離 해내고 EDAX로 이를 分析하였으며, 이들 結果를 要約하면 다음과 같다.

nitrate solution method를 適用하면 YBCO系에 있어서 비교적 短時間에 緻密한 微細組織을 갖는 遷移 溫度 90K의 超電導體를 製造할 수 있다. Meissner효과를 이용하여 고천이온도에서 抽出해낸 미소영역의 EDAX分析 結果는 固相法을 사용한 YBCO-23S와 nitrate solution method으로 製造한 YBCO-23N 및 YBCO-36N 에서는 초기의 組成과 거의 같았으며, 고천이 온도에서 추출된 미소영역은 조성보다는 산소 결함의 차이에 기인한 것으로 생각된다. 共沈法으로 製造한 YBCO-23NA 에서는 과도한 Ba의 組成을 보였으며, 천이온도 100K 인 Bi계에서는 약한 반자성효과 때문에 추출이 불가능 하였다.

Introduction

A workable high temperature superconductor could make possible a number of technological applications: from super-powerful motors and propeller-less ocean ships to zero-loss electric transmission and magnetically levitated trains. Many have compared its potential with discovery of the transistor 40 years ago[1].

The research for high-Tc superconducting oxides was triggered by the discovery of superconductivity above 30K in the La-Ba-Cu-O system by Bednorz and Müller[2] and further excited by superconducting transition temperature in excess of the boilling point of liquid nitrogen, superconductivity at 90K, in the Y-Ba-Cu-O system by Wu et al.[3] Since then intensive studies have been made to increase the critical temperature of superconductivity and to clarify the mechanism of these oxide material and also to find other new family of superconducting oxide material. As the results, new superconducting materials were found by Maeda et al.[4] in the Bi-Sr-Ca-Cu-O system at

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110K and by Sheng and Hermann[5] in a Tl-Ba-Ca-Cu-O system at 125K[6] without rare earth materials, respectively.

It has been reported that the superconductivity properties of these system are related to the oxygen -deficient perovskite crystal structure. The order -disorder of the oxygen atoms in the Cu(1)-O layer between two layers(ie. Ba in YBCO) is believed to be the principal reason for the phase transition from the orthorhombic to the tetragonal phase[7]. However there are important problems to be solved, that is, how to obtain a specimen of high quality, the preparation conditions which influence on the superconducting properties of the specimen..

Standard solid-state reaction process for synthesizing High-Tc ceramic superconductor involves mixing oxides of the constituent elements, followed by subsequent heat treatments at temperatures of 900 - 1000℃. However, the volume farction of the resulting superconducting phase in the oxides ceramic thus prepared generally amounts to only about 20-30%, indicating the difficulty in achieving a homogeneous single - phase material. Other methods involving chemical synthesis reaction, ie. coprecipitation method. The advantage of the coperecipitation method is that the constituents are mixed on an atomic scale which helps in the formation of the desired phase. Unfortunately, they also yield material with more of less the same volume fraction of the superconducting phase of the solid state reaction process[12].

A large number of efforts have been made on synthesizing procedures of these oxide superconductors, ie. coprecipitation method[9),10], sol-gel process proposed by Kordas et al[8]. Kishida et al.[11] prepared sample from starting of Y_2O_3, $Ba(NO_3)_2$, $Cu(NO_3)_2$ and Y_2O_3, $BaCO_3$, CuO, and reported that the nitrates series were more closely packed and higher Tc was shown.

In this study, $LaBa_2Cu_3Oy$, $Y\ Ba_2Cu_3Oy$, $Bi_{0.8}Pb_{0.2}Sr_{0.8}Ca_4CuOy$ were prepared in various processes, solid - state reaction method, coprecipitation method and namely nitrate solution method. Samples prepared by the nitrate solution method were compared to the other ones by means of X-ray diffraction analysis, electrical resistance measurements and microstructural examination through scanning electron microsocope with EDAX device. The isolation technique[13] is used on the prepared materials to isolate small particle, the micro region which shows probably higher-Tc among the regions. The isolated particles were chemically analyzed by X-ray energy dispersive spectrometry to identify the composition of the particle.

Materials and Experimental Procedures

Several processing procedures, solid state reaction, coprecipitation and nitrate solution method, have been applied to synthesize high Tc superconductors of La-Ba-Cu-O, Y-Ba-Cu-O and Bi-Pb-Sr-Ca-Cu-O system in this study.

For solid-state reaction method, nominal composition of $LaBa_2Cu_3Oy$(LBCO-S), $YBa_2Cu_3O_y$(YBCO-23S) and $Bi_{0.8}Pb_{0.2}Sr_{0.8}Ca_4CuO_y$ (BPSCC) were prepared by mixing the appropriate amounts of oxides (Bi_2O_3, CuO, La_2O_3, Y_2O_3, PbO) and/or carbonates($BaCO_3$. $CaCO_3$, $SrCO_3$) of component metals and calcining the mixtures at 920℃ for 3h in case of YBCO, and 950℃ for 3h in case of LBCO and 800℃ for 3h in case of BPSCC. After being reground, each calcined powder was pressed and sintered for 10h at 950℃ for YBCO, 10h at 1000℃ for LBCO and 72h at 850℃ for BPSCC, then slowly furnace cooled to room temperature. The specimens were then annealed at the temperatures as described in Table 1.

The samples of YBCO-NA were prepared by a

coprecipitation method from aqueous solution of Y, Ba, and Cu nitrates, followed by a solid-state reaction and decomposition of the precipitates at 950℃, and Na_2CO_3 was used to initiate the precipitation.

In nitrate solution method for Y-Ba-Cu-O system(YBCO-23N and YBCO-36N), high purity(99.9%) powders of $Y_2(NO_3)_2 \cdot 6H_2O$, $Ba(NO_3)_2$, $Cu(NO_3)_2 \cdot 3H_2O$ were used as starting materials. The reagents were weighed so that the stoichiometric ratio of Y, Ba and Cu was equal to 1:2:3 and 1:3:6 for YBCO-23N and YBCO-36N, respectively. These were dissolved in appropriate amount of deionized distilled water in the ratio of 0.1 mol each and stirred to mix well at the ion level. Therefore, the pH value of the final solution could be adjusted to 4.5. The solution was firstly heated slowly up to 500℃ in an open crucible furnace in air so as to dehydrate and eliminate nitrate group. A Pyrex beaker was used as a container in the furnace.

The dark brown resultant reasidues were collected and pulverized and then calcined at 920℃ for 3hr in oxygen flowing atmosphere at heating rate of 200℃/hr. The calcined powders were homogenized by grinding again and cold pressed in to a pellet 12mm in diameter and about 2mm thick under the pressure of about 10,000Kg/cm². The pellets were sintered at 950℃ for 6hr in a quartz tube furnace. The quartz tube was used to help the reduced oxygen pressure condition with the flow rate of 100ml/min.

Disk-shaped samples were cut in the rectangular dimension of the order of a few millmeters with length-to-width ratio of 8:1 or higher to measure the electrical resistance. The current and voltage leads were attached to the specimen using the silver paste. The standard four-point-probe measurement was performed with changes in the polarity of current. Silver wires were used as probe and constant current of 5mA was applied. The measurement was performed in a continuous-flow cryostat connected to a microcomputer to give fully automatic system for temperature variation, data acquisition and processing.

Powder X-ray diffraction measurements at room temperature were carrid out with a Rigaku diffractometer to identify the crystal phase of the obtained products at 0.06 degree interval for 1 sec over a range from 20° to 70° of 2θ with Ni filtered Cu Kα radiation.

The isolating technigue, a microscopic meissner effect, involves powdering of the superconducting samples in size of 10-30um approximately and placing the powders on a flat area of sample holder. The sample holder was made of very thin, 0.1mm thick, glass. This glass holder was kept from the moisture to minimize the water condensation problem during the isolation. Even though the temperature ot the holder could be monitored with a thin thermocouple, it was not enough to measure the temperature of each particle due to the variation of temperature in the holder. Therefore the critical temperature of the isolated particles are ignored in this research.

In isolation process only a few particles which showed strong repulsion firstly against the applied magnatic field among the powdered sample in holder were taken out under the microscope as the isolated particle. As a picking device, an extremely fine glass needle with epoxy tip was used.

Bulk and isolated specimens were fixed in epoxy resin and mechanically polished with carborundum and diamond paste to examine the microstructure and element analysis. Chemical composition analysis was performed on the bluk and isolated particles of Y-Ba-Cu oxide using a technique of the energy dispersive spectrometry(EDAX).

Table 1. Summary of process conditions, nominal composition and Tc of specimens

samples	nominal composition	process method	calcining	sintering	annealing	Tc
YBCO-23S	YBa_2Cu_3Oy	solid reaction	920℃	950℃	500℃	~90K
YBCO-23N	YBa_2Cu_3Oy	Nitrate Solution	920℃	950℃	none	~90K
YBCO-NA	YBa_2Cu_3Oy	Carbonates coprecip.	920℃	950℃	none	~76K
YBCO-36N	YBa_3Cu^6Oy	Nitrate Solution	920℃	950℃	none	~78K
LBCO-S	$LaBa_2Cu_3Oy$	solid reaction	950℃	1000℃	350	~72K
BPSCC-S	$Bio._8P_{0\cdot2-}$ $Sro._8CaCuOy$	solid reaction	800℃	850℃	none	~100K

Results and discussion

The obtained samples were primarily characterized by the powder X-ray diffraction (XRD) analysis at room temperature.

The XRD spectra of $YBa_2Cu_3O_y$ (YBCO-23S, YBCO-23N, YBCO-NA), $YBa_3Cu_6O_y$ (YBCO-36N), $LaBa_2Cu_3O_y$ (LBCO-S), and $Bi_{0.8}Pb_{0.2}Sr_{0.8}CaCuO_y$ (BPSCC) prepared in different synthesizing processes as described in experimental procedures are shown in figure 1, respectively. Sample of YBCO-23S of Fig.1(a), which was prepared by the solid-state reaction method shows the orthorhombic state of the high transition temperature superconducting $YBa_2Cu_8O_{7-x}$ phase, as indexed by specific reflection indices.

The position of XRD patterns of YBCO-23N in Fig.1(b) which is prepared by the nitrate solution method nearly coincide with those of YBCO-23S of Fig. 1(a). This fact indicates that there is no significant differences in XRD patterns between these two samples due to the difference in preparation methods. However, YBCO-NA of Fig.1(c) Which is prepared by carbonate coprecipitation method showed big differences even though the nominal composition was same. The XRD patterns of YBCO-NA and YBCO-36N (nitrate solution method) are almost identical each other as shown in Fig.1(c) and (d), respectively. In these two samples, there were some diffraction peakes, at $2\theta = 29.16°$, 29.47° and 29.94° attributtable to extra peakes and the relative diffraction intensities are more decreased in YBCO-36N and YBCO-NA samples compare to the samples of YBCO-23S, YBCO-23N. The extra phase was confirmed due to the formation of crystalline phase of $BaCuO_2$. The formation of crystalline phases of $BaCuO_2$, CuO or Y_2O_3 could be influenced by the raw material and heat treatment, ie. calcination effect[14]. This indicates that the volume fraction of high-Tc phase in YBCO-36N and YBCO-NA is much smaller than the YBCO-23S and YBCO-23N.

Fig. 1(e) shows the XRD patterns of LBCO-S prepared by conventional solid reaction method : temperature of 1000℃ for 10 hours and followed annealing at 350℃ in flowing oxygen for 5hr is almost similar to that of observed for YBCO-23S and YBCO-23N. In the preliminary test, it has been found that the sample preparation by the coprecipitation

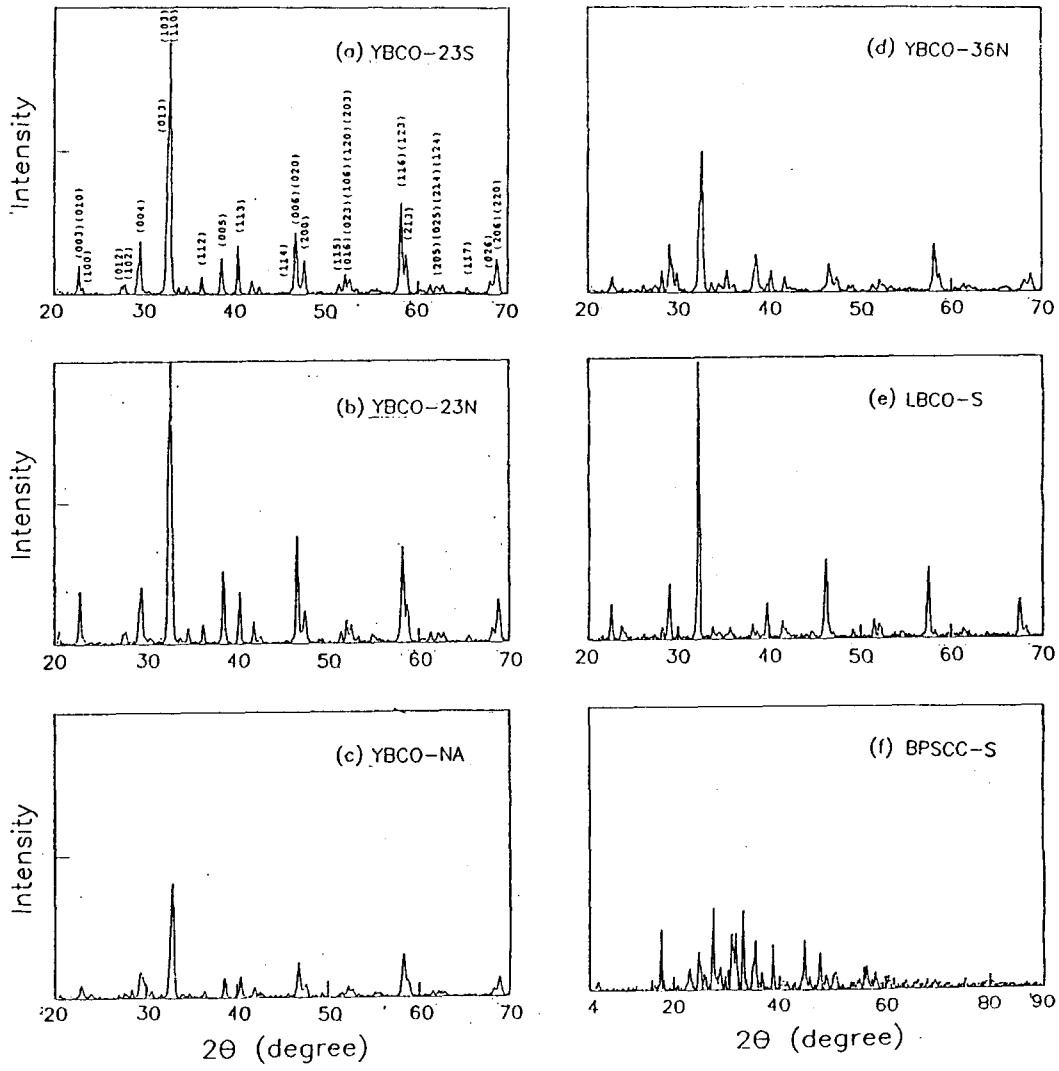

Fig.1. X-ray differaction patterns of specimens : a) nominal composition of $YBa_2Cu_3O_y$ by solid reaction method, b) nitrate solution method, c) coprecipitation method in Na_2CO_3, d) composition of $YBa_2Cu_3O_y$ by nitrate solution method, e) composition of $LaBa_2Cu_3O_y$ by solid reaction method, f) Bi-Pb-Sr-Ca-Cu-Oby solid reaction method.

method and the nitrate solution method for LBCO system were not succeed to obtain high Tc in resistance measurement. The same result was reported that for the $La_1Ba_2Cu_3O_y$ series, the solid state reaction method produces sample with higher Tc's than the coprecipitation method, in spite of the fact that the solid-state reaction method always seems to result in samples with other phase present while the coprecipitation method does not[15].

X-ray patterns of solid reactioned Bi-Pb-Sr-Ca-Cu-O are shown in Fig.1(f). Nitrate solution method on this system was not successful due to the soluability of $Bi(NO_3)_2$ into water. Therefore, these samples, LBCO and BPSCC by coprecipitation and nitrate solution method were no longer considered in this paper.

The temperature dependence on the electrical resistances of the specimens prepared in various processing procedure are shown in Fig.2. The samples of YBCO-23S and YBCO-23N exhibited the highest value of around 90K in resistance measurements. On the other hand, YBCO-NA and YBCO-36N show their resistance around 76 K and 78K, respectively. The samples of LBCO-S and BPSCC prepared by solid reaction method showed around 70K and 100K, respectively. For LBCO-S, the annealing was carrid out very low temperature around 350℃ for 5hr. These all results obtained from the resistance measurements were well matched with the results of the X-ray diffraction analysis. The difference in the resistances among these samples may be due to the second phase such as $BaCu_2O$ and a slight differences in the O vacancies on the orthorhombic phase to tetragonal phase fomation. The results of resistance measurements are summarized in Table 1.

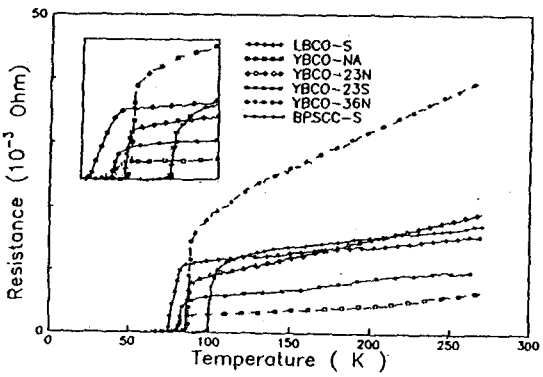

Fig.2. Resistances of LBCO-S, YBCO-NA, YBCO-23S, YBCO-23N, YBCO36N and BPSCC as a function of temperatures. YBCO-23S and LBCO-23S are prepared by solid reaction method, and YBCO-23NA is prepared by copre cipitation method in Na_2CO_3, YBCO-36N and YBCO-23N are for the specimen prepared by nitrate solution method.

Fig. 3-6, Shows a series of scanning electron micrographs(SEM) and the spectra of X-ray energy dispersive analysis(EDAX) on the polished surface of each sample. For quantitative snalysis, three different grains in an area were chosen for examination to identify the composition of the isolated particles.

In Fig. 3, The microstructure of the polished surface of YBCO-23S which is prepared by the solid state reaction method with nominal composition of $YBa_2Cu_3O_y$ is shown. The reacted compound were composed of grains whose sizes are of several microns to several tens of microns. In the microstructure, the striations are formed as twin structure. These twins are introduced during the phase transformation : the high temperature tetragonal phase transforms to the orthorhombic phase when the specimen is gradually cooled in the furnace. The orthorhombic distortion is caused by oxygen vacancy ordering in the (110) direction on Cu-O atomic planes which are located between two adjacent Ba-O atomic planes on (001) planes. It is well known that the elastic energy associated with the nucleation of phase transformation can be mininized by taking a thin lenticular shape of

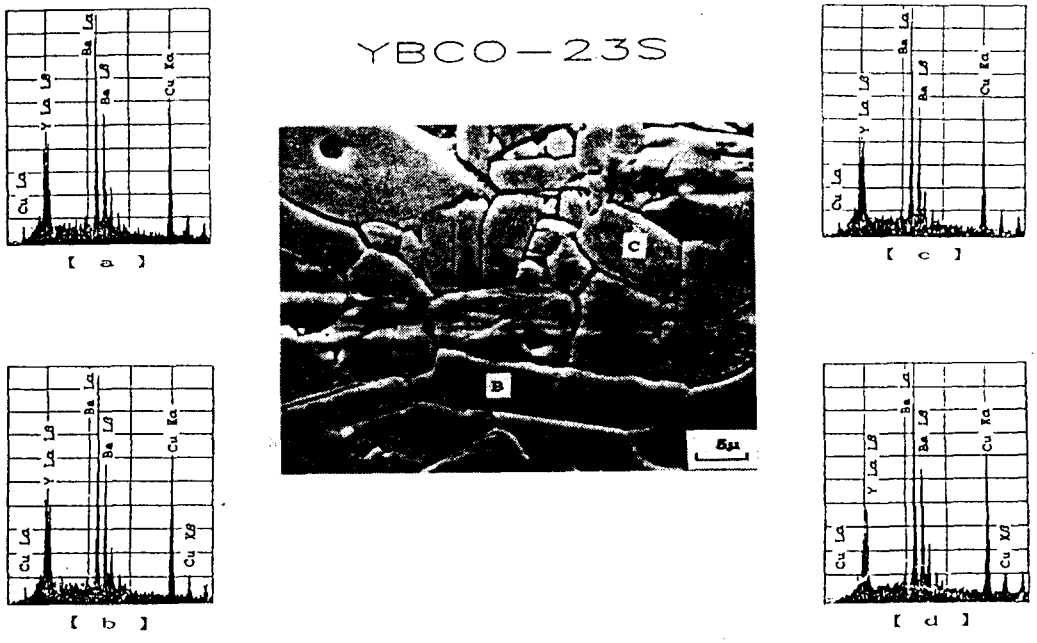

Fig.3. Scanning electron micrograph and X-ray energy dispersive analysis spectra of a sample prepared by solid-reaction method with a nominal composition of $YBa_2Cu_3O_y$. The spectra of a), b), c) are the signals from the corresponding positions of A, B, C. In the photo, striations due to twin are shown.

the orthorhombic phase. In addition, the overall elastic energy for a macroscopic size of new orthorhombic phase can be reduced by taking the twinned structure in the orthorhombic phase[17].

Fig. 4, shows a scanning electron micrograph and the EDAX spectra from different grains of YBCO-23N, which is prepared by nitrate solution method. The micrograph shows very densed microstructure and the spectra of EDAX shows the starting composition of $YBa_2Cu_3O_y$.

Fig. 5, shows SEM and EDAX spectra from grains of YBCO-36N, which is prepared by nitrate solution methed. Very coarsed microstructure is seen and the spectra of EDAX shows the starting composition of $YBa_3Cu_6O_y$. In Fig.6, however, the composition analysis shows that the grains are composed of Ba-rich structure compare to the starting compositions of YBa_2CuOy. It has been also found that the micro regions of compositions are far from the ideal values, especially the barium content is quite higher than the suspected amount in the Fig.6 of carbonate coprectipitated sample.

In order to confirm the occurrence of the higher Tc superconductivity, it is indispensable to observe the existance of the perfect dimagnetism. This principal concept has been used in the isolation technigue, the application of the perfect diamagnetism was used to spererate the possibly higher-Tc superconducting particles in the powders of the synthesized samples. In the isolation process, the thin glass sample holder containning mono layerly spreded particle is cooled carefully using liquid nitrogen and applied strong magnetic field by closing the glass holder to a 0.24T of Sm_5Co magnet which is already cooled. This procedure tended to move the particles, and thus the particle of sample that exhibited the perfect dimagnetism at higher temperature than the others is successfully

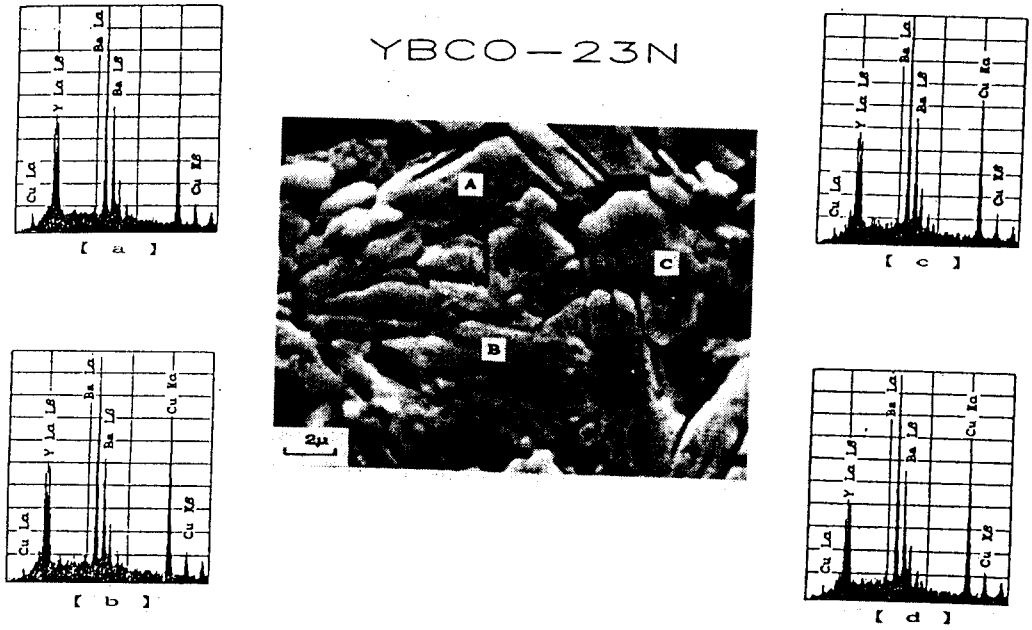

Fig.4. Scanning electron miorograph and X-ray energy dispersive analysis spectra of a sample prepared by nitrate solution method with a nominal composition of $YBa_2Cu_3O_y$. The spectra of a), b), c) are the signals from the corresponding positionsl of A,B,C.

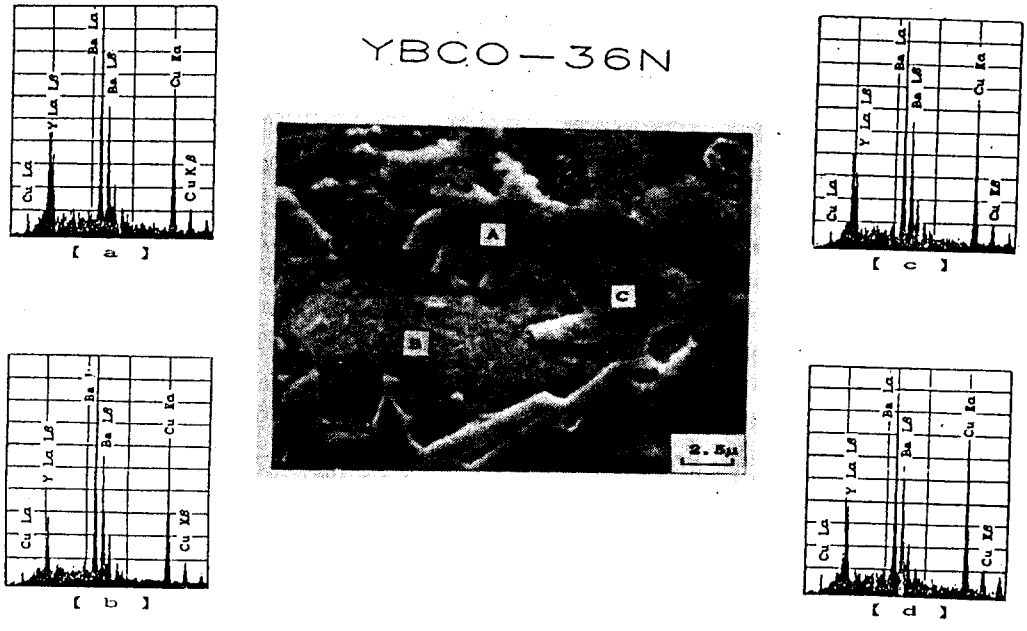

Fig.5. Scanning electorm miorograph and X-ray energy dispersive analysis spectra of a sample prepared by nitrate solution method with a nominal composition of $YBa_3Cu_6O_y$. The spectra of a), b), c) are the signals from the corresponding positionsl of A, B, C.

isolated.

The bulk and isolated samples were analyed by dispersive X - ray micro - analysis. X - ray intensities from the irregular surface of the small particle exposed to the electron beam could imply significant errors due to the geometric effects[18]. To eleminate such deficiences in the measured compositional values during the chemical analysis, surfaces of the epoxy-mounted particles and bulk sample were flattened by means of mechanical polishing. An isolated particle which is flattened is shown in Fig.7(a). with the results of the composition analysis by means of EDAX spectra on the isolated particles of YBCO-23S(b), YBCO-23N (c), YBCO-36N(d) and YBCO-NA(e). From the quantitative analysis, which is sensitive only to heavier elements, it is confimed that no elements other than Y Ba and Cu were detected within the sensitivity of detector. Mean values of the ratio among the three metal elements, Y, Ba and Cu were identical to the starting nominal

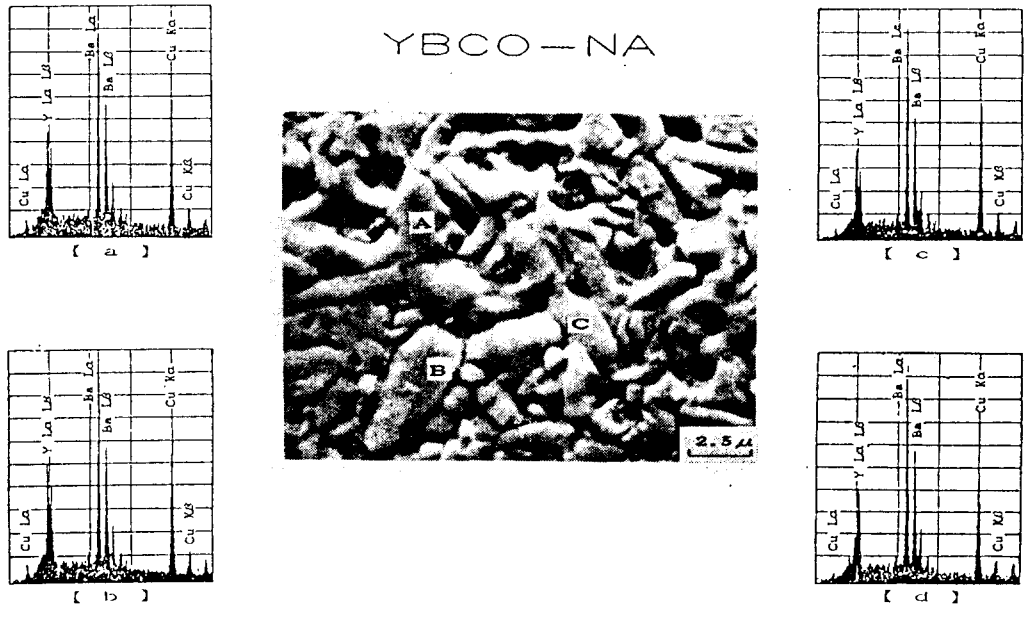

Fig.6. Scanning eleotron miorograph and X-ray energy dispersive analysis spectra of a sample prepared by carbonate coprecipitation method with a nominal composition of $YBa_2Cu_3O_y$. The spectra of a), b), c) are the signals from the corresponding positions of A, B, C.

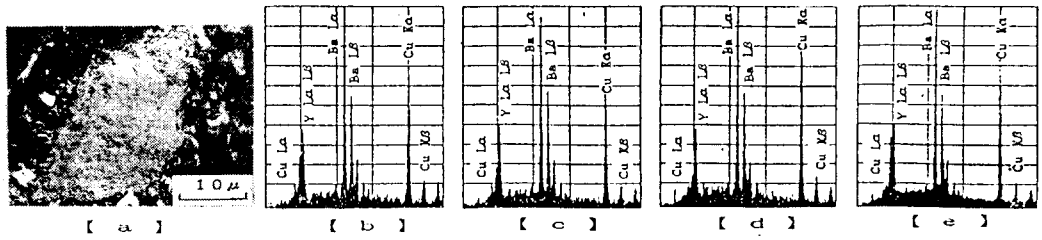

Fig.7. Scanning electron miorograph of an isolated partcel (a) whose surface is flattened and the energy dispersive X-ray spectra of the isolated particles with starting nominal composition of $YBa_2Cu_3O_y$ for YBCO-23S(b), YBCO-23N(c), YBCO-NA(d) and $YBa_2Cu_3O_y$ for YBCO-36N(e)

compositions of YBCO-23S(b), YBCO-23N(c), YBCO-36(d), however in case of YBCO-NA(e), Ba-rich phase were found.

Superconductivity can be confirmed by checking the zero resistance and the perfect dimagnetism together. Therefore, the zero resistances of the isolated also need to be tested. However it is extremely hard to measure the resistance of such a small particle due to the difficulties in the electrical contact of the electrodes to the samples. Isolation of micro regions having higher Tc in La-Ba-Cu-O and Bi-Pb-Sr-Ca-Cu-O system could be important from the technological point of view. Therefore studies are under way to identify the superconducting high Tc phase, as well as to analye micro regions in La-Ba-Cu-O and Bi-Pb-Sr-Ca-Cu-O system.

Conclusion

In conolusion, a high-Tc superconducting $YBa_2Cu_3O_y$ phase with zero resistance at about 90K was successfully prepared by nitrate soultion method with densed micro structure The result of the EDAX analysis on the isolated particles using the microscopic meissner effect showed that the particles were isolated at higher temperature due to the differences in O vacances rather than the differences in chemical compositions. The compositions of the isolated particles were almost identical to the starting compositions on the samples prepared by the solid reaction and nitrate solution method but the Ba-rich compositions were seen in the coprecipitated sample. The isolation process on Bi system was not successful due to the weak dimagnetism even though its high Tc above the liquid nitrogen temperature.

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