マイスナー効果を直視する高 Tc の観測

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The Observations of the Tc Confirmed with the Meissner Effect Signal

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Abstract:
There has been considerable controversy over the measured points of superconducting transition temperature (Tc) since especially in 1986. Some of them have possibly arisen through premature attempts to generalise about cooling treatment from the results of limited experiments. This paper introduces my own method of simplified procedure to measure the Tc of the Y based copper oxides and the focus of attention is the observations of the higher Tc confirmed with the Meissner effect signal. The results suggest that the noticeable advances are made in understanding and improving the method of Tc detection.

I. Introduction

Although the Tc is not the only criterion for determining the technological usefulness of a superconductor, the proper method of detection of Tc that will impart desirable properties and physical phenomenon is essential to realize significant technological applications. Remarkable advances have been made in understanding and improving the behavior of high-Tc superconductors (HTS) by numerous researchers in various parts of the world over the last ten years. So far, no one has been able to obtain the Tc higher than 173K (−100℃) as far as I know, but these efforts should be continued to come because of the enormous potential scientific and technological pay-off. In this study, I examined the processing and properties especially for Tc of the Y based copper oxides that offer high potential for operation at liquid nitrogen temperature.

II-A. Processing of HTS Samples

First of all, The brief paper[1] by D.T.Shaw and S. Jin published in 1993 is the significant effective aspects giving current status on the processing of HTS samples. They describe it there as follws. The HTS compounds such as YBCO is mechanically brittle ceramic materials, and is generally prepared during the early stage of fabrication by powder processing. Since the driving force for densification of powder compact is the reduction of the free energy associated with the free surfaces of the particles, the HTS materials are usually processed from finely divided powders for efficient consolidation. Processing of the bulk ceramic materials can be devided into three steps such as powder preparation, shaping, and sintering. Conventional techniques for the ceramic powder preparation or some modified versions are also used for the HTS materials. For example, YBCO powders are prepared by mechanical mixing of precursors, such as hand grinding using mortar and pestle in the laboratory or ball milling. The precursors could be in the form of oxides, nitrates, carbonates or other compounds containing the component metals of the superconductor. Ball milling is generally carried out in an aqueous medium. If one or more of the precursor materials tend to react with water, other media such as acetone or alcohol should be used instead of water. After sufficient ball milling, the milling medium is removed either by filtration or spray drying. The dried powder is calcined at high temperatures to facilitate the decomposition of the precursors to oxides and to allow diffusional mixing for the formation of the stoichiometric superconductor phase. If necessary, the process of calcining and grinding may be repeated several times for further chemical homogenization. A number of other powder preparation techniques have also been utilized for HTS materials. However, the sources of HTS samples used in this study were as follows: Y_2O_3, $BaCO_3$, CuO and acetone from Isekyu, Nagoya.

II-B. Shaping of HTS Samples

HTS for bulk application, such as magnetic bearings, microwave cavities, or persistent current permanent magnets, could have a number of different configurations (e. g, blocks, rods, sheets, cylinders, etc).

The most common method of shaping bulk HTS materials is by dry prresing, which involves filling a metal die (either closed die or extrusion die) with HTS powder, and pressing at 100~500(MPa) with a plun ger. A small amount of organic binder is often added to the powder for lubrication and to improve the strength of the compact. The powder compact of YBCO is then sintered by slow heating and holding at 900~950 (℃) for 5~100 (hours) in an oxygen atmosphere or partial oxygen atmosphere. This is followed by slow cooling to render the optimum oxygen stoichiometry and the highest Tc. The optimal sintering temperature for the BSCCO and TBCCO superconductors are lower (below~850℃) than those for YBCO(1).

If the density of sintered YBCO is too high, the oxygenation treatment has to be extended in order to allow sufficient time for the diffusion of oxygen into the material. The Jc value of YBCO is low when the sintering is carried out at temperatures below ~890 (℃)(1).

This is due to the poor connectivity between the superconductor particles in the sintered material. Sintering at intermediate temperature of 900~950 (℃) gives a porosity of about 85~90 (%) and considerably higher Jc. Above about 950 (℃), the Jc value deteriorates again(1). This is due to the difficulty in oxygenating dense materials and to the occurrence of some microcracking. Shock compaction has also been used for the shaping of YBCO type superconductors. Shock waves, usually generated by detonation of explosive, can apply a dynamic pressure of several gigapascals on the superconductor powder compact and produce dense materials. This technique could achieve shaping and densiflcation of large mass pieces, but may be cumbersome for mass production of small bulk parts. A typical problem encountered in the shock wave loaded YBCO is the suppression of Tc, which may be caused by either disturbed crystal lattice structure or microfragmentaion(2). Extensive sintering heat treatment above 900 (℃) is required to restore the value of Tc to about (−183℃). Bulk HTS an also be fabricated by press forging(3). Because of the high pressing temperature close, to the solidus or the partial melt temperature (about 1000℃ for YBCO), sufficient plasticity is induced in the normally brittle ceramics to allow slow deformation under sustained pressure. The disadvantages of this technique include slow speed (several hours of pressing) and high temperature operation. An interesting observation that has been made with this technique is the formation of strong texture (c axis parallel to the pressing direction) on the surface layer, which is several microns thick.

This layer exhibited an improved Jc value of more than 3000 (A/cm^2)(1), with reduced field dependency.

Although it is not clear how the high temperature plasticity can be utilized to produce practical high-Jc bulk or wire superconductors. But the factors of shaping used in this study were as follows: cylindrical blocks (ϕ28, t: 3~4), dry pressing at 95 (MPa), acetone (as the organic binder), holding at 900 (℃) for 22h45m in an oxygen atmosphere.

II-C. Phase Equilibria in the Y-Ba-Cu-O System

In fact, sintering of HTS samples is an one kind of heat treatment. There for, In order to design the samples, it is useful to discuss the phase equiliblia in the Y-Ba-Cu-O system. On that subject, the paper(4) by R.J.Cava becomes reference standards. That is, there are many circumstances in the processing of the 1, 2, 3 superconductor where detailed knowledge of the temperature-composition-phase assemblage characteristics of the system Y-Ba-Cu-O are of interest. It is especially of interest in any processes in which single phase material, crystal growth, or precipitation of the 1, 2, 3 from a melt. Most importantly, many studies have shown that the 1, 2, 3 phase is not a congruent melter for any rare earth under any oxygen partial pressures attempted for synthesis.

This is very strong limitation on the size of crystallites that can ultimately be grown from a Y-Ba-Cu-O melt. Further, a primary phase field for the 1, 2, 3 compound has never actually been observed, although its existence somewhere in composition-temperature space has been proposed by many. This means that there are at present no known conditions where the 1, 2, 3 compound is the first phase to precipitate on cooling a melt of Y-Ba-Cu-O. This clearly further complicates any process where crystals of 1, 2, 3 are a desired product.

Infact, for crystal growth of 1, 2, 3 from Ba-Y-Cu-O melts, crystals are very often grown on surfaces or in cavities strongly suggesting that their growth is not throuh conventional precipitation from the melt.

There are two complications which make the study of the Y-Ba-Cu-O chemical system under the usual synthetic conditions quite interesting, they are: (1) the oxidation／reduction of copper, which makes the copper oxide vertex in a conventional Y_2O_3-BaO-CuO diagram actually $CuO_{1\pm x}$ and (2) due to the presence of Ba and the CO_2 in air, there is really always a CO_2 vertex if CO_2 is in the starting materials or the reaction is done in air. The other perovskite near the composition $Ba_3YCu_2O_x$ in the BaO-Y_2O_3-CuO system is actually an oxycarbonate, with CO_2 an integral part of the structure, and is not present under synthetic conditions which rigorously exclude CO_2.

R. S. Roth and his coworkers have studied the Ba-Y-Cu-O phase equilibria diagram in detail(5). And R. J. Cava presents their data in the figures(4) of phase equilibria (Other groups also looked at the phase equilibria in this system but R. J. Cava selected work from a single group for internal consistency).

Note that compounds in the dlagram(4) are labeld by atomic ratios in the order Ba : Y : Cu which is crystal chemically correct, rather than the now common Y : Ba : Cu. Thus the 1, 2, 3 compound is labelled at 2, 1, 3 in his set of figures(4) One of them shows the general ternary diagram at 950℃ in air. The compatibility triangles were determined by making samples in each region. (For a general composition in a ternary system the three phases present are those at the corners of the triangle on the figure which bounds the composition. For compositions on the tie lines which difine the triangles, the two phases present are those at the ends of the line.) The three ternary compounds are shown as $BY_2C=BaY_2CuO_5$ phase, $B_2YC_3=Ba_2YCu_3O7$, and $P_{SS}=$ the other perovskite which is a solid solution of the formula $Ba_{3.2}Y_{0.8}Cu_{2-x}O_{6.4-x}\cdot ZCO_2$ where $0.1\leqq X\leqq 0.3$. This compound is bounded by, but does not include the compositions (Ba : Y : Cu) 3 : 1 : 2, 4 : 1 : 2 and 5 : 1 : 3. It can not be prepared in rigorously CO_2－free synthetic conditions. The figures which show the temperature-composition profile are pseudo-binary cuts across triangular figure with some lines to show the evolution of the phase equilibria with temperature in air. Experimental points seem to be shown. And R. J. Cava says that the complexity of the system is apparent and such diagrams are not only useful knowledge necessary for knowledge of the physical state of different materials of various compositions at different processing temperatures, but also for defining good conditions for crystal growth, In figue of T-C profile for instance, a good primary phase field for crystallization of BaY_2CuO_5 from a melt between 1200～1000 (℃) is defined(4). The melting relations in the vicinity of the superconducting composition $Ba_2YCu_3O_7$ in air are of paticular interest. $Ba_2YCu_3O_7$ melts through a four phase region in air, requiring that the system contains four components under these conditions, not three. This implies that CO_2 is present in some of the phases: the likely culprits are the liquid phase and one or more of the solid phases $BaCuO_2$, $Ba_2YCu_3O_7$ or BaY_2CuO_5, although one would assume that significant quantities of CO_2 would have been detected in 1, 2, 3 by now if that were indeed the case. This suggests at least that $BaCuO_2$ is the most likely solid phase with significant CO_2 content under these conditions. The detailed phase equilibria in the vicinity of 1, 2, 3 considering the implied presence of CO_2, are presented in the figure showing near $Ba_2YCu_3O_x$. The other cut is designed to explore the melting relations in the composition region of the other perovskite, In the figure showing T-C profile, he suggests the primary phase fields for the Ba-Y-Cu-O system too. The primary phase field encloses the compositions where the phase indicated is expected to be the first phase to precipitate from the melt. This is critical information for crystal growth and melt processing of ceramics. Note the disastrous displacement of the 1 : 2 : 1 BaY_2CuO_5 phase field to the BaO-CuO rich region of the diagram. This strongly impacts the melting of 1, 2, 3 for which a thin sliver of a primary phase field has been drawn. This $Ba_2YCu_3O_7$ primary phase field is included, however, only to satisfy thermodynamics and has never been observed, neither by Roth nor by anyone else working on this system. Even if the tiniest sliver does truly exist and can be found in the future, it is not likely to be of practical importance due to its undoubtedly extremely narrow composition ／ temperature characteristics(4).

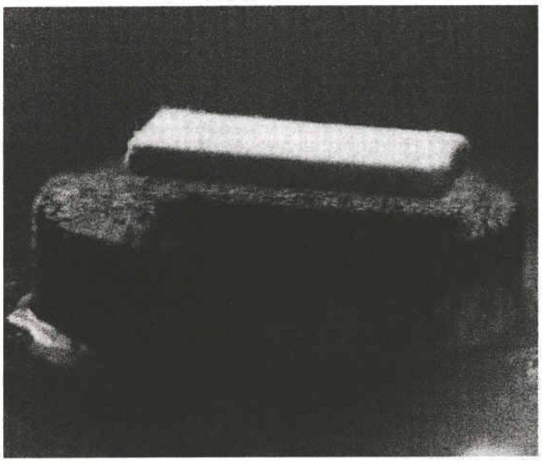

Fig 1, The magnet of 0.4 (T) is floating on the K1 type HTS at the special temp'90℃

III-A. The Observations of Tc at K 1 Type HTS

On referring to some aspects and criteria above mentioned, We can produce the K 1 type HTS(6) samples which seem to suggest the higher degree of superconductivity in this field. And here, I can introduce them as the examples of K1 type sintered conductors(6) to investigate the Tc and its Meissner effect signal. As we can see in the fig. 1, the magnet of 0.4 (T) is floating on the K 1 type sintered conductors. This suggest that the conductor must be HTS because of its magnetic floating observed at the temperature. The temperature around the conductor is temporarily cooled approximately equal to (−) 196℃ by pouring liquid nitrogen into the vessel.

After filling up with the liquid nitrogen over the top of the conductor, the liquid nitrogen in the vessel evaporates in the air and a few minutes later the temperature around the conductor raises rapidly. On the rising way to the room temperature, the wooden pedestal(6) makes slow down the rising rate of the tem-

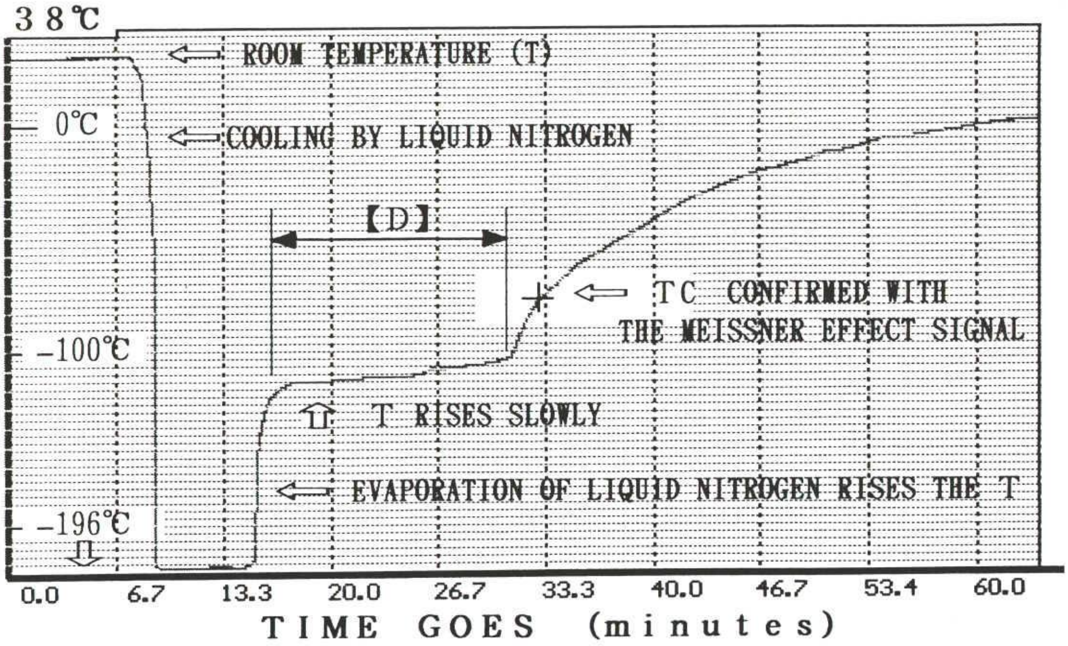

Fig 2, The wooden pedestal makes a convenient domain [D].

perature and makes a convenient domain to investigate the Tc. As we can see it in the Fig. 2, the domain is labelled at 【D】 and is in the range of (－) 150≦D≦(－) 100℃ as far as I examined with digital thermometer. Therefore, if the Tc of the HTS is in that range of (－) 150≦D≦(－) 100℃, we should be able to observe the magnet falling down slowly to the upper surface of the pedestal. And taking a good look at there, we should be able to observe the Tc on the Meissner effect signal almost at the same time.

That is to say, this is the method of Tc observation in this paper and making use of this method. I examined the Tc of K 1 type HTS. And the results are plotted in Fig. 2. Furthermore, as you can see , the Tc is observed to be higher than about (－) 100℃! This is an abnormal Tc isn't It? I have never heard such a higher Tc yet. Still more, the observation which makes use of digital thermometer shows that the Tc is about (－) 90℃ (183K!). It's an incrediblel, but is the experimental results in this paper and, I'm sure this is the special Tc since the discovery of superconductivity in 1911 if the method of experiment is in correct.

III-B. Observation of Zero Resistivity

As a matter of fact, It is troublesome to detect the zero resistivity because the small resistance such as a contact resistance, connecting wire's, and some electrical noise are usually in existence. Considering all possible items relating to observation of zero resistivity, I observed the voltage at the constant DC current instead of the resistance. In the Fig. 3, the vertical axis express the voltage which occurs at the inspectional points A, B in the circuit. As you can see in the Fig. 3, if the resistive components of the device change one after another, the voltage at AB reasonably changes too. That is to say, the resistivity of the HTS is very small and is less than 10 [Ω／AB] at the room temperature. And further the observations in the Fig. 3 suggests that the resistivity of the HTS (especially K 1 type)⁽⁶⁾ is sufficiently small and is worthy of notice.

IV. Conclusions

The K 1 type HTS was first made by accidental sintering treatment in this work at the end of the July in 1997. Even in those days, this accidental HTS sample was showing some abnormal resistivity and higher degree of superconductivity, but I didn't have any confidence in the experimental observations because of its abnormality indeed. After the events, I tried to create the K 1 type HTS samples systematically and have been investigating their physical behaviors, abnormal

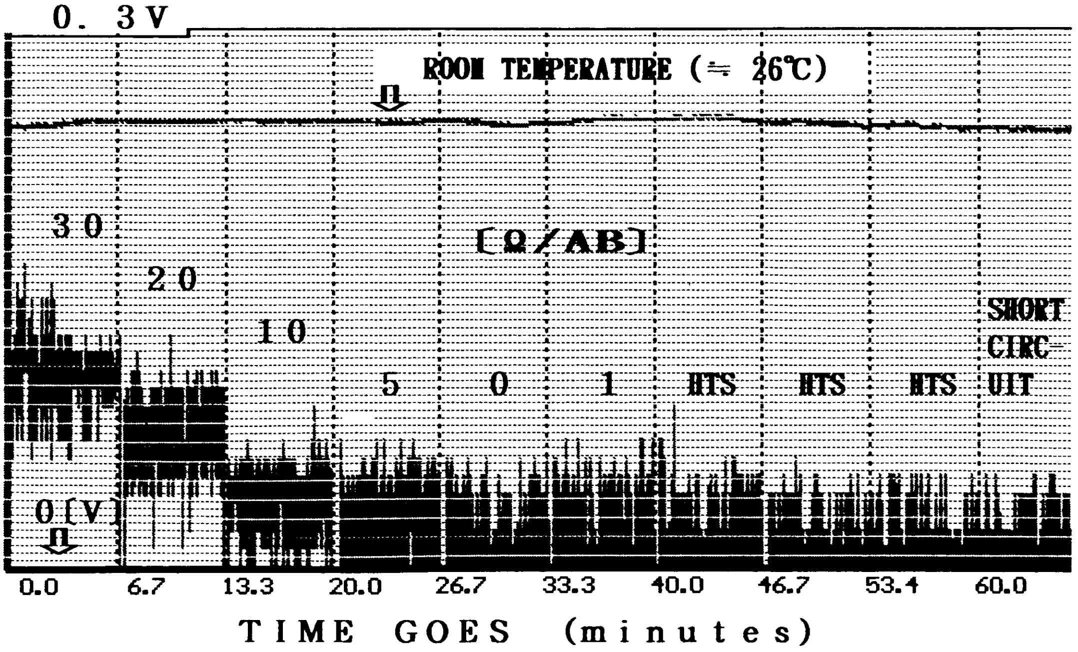

Fig 3, The resistance of the K 1 type HTS is sufficiently small and is worthy of notice.

Tc and zero resistivity especially. So far the results are:

(1) The Tc and zero resistivity of the K 1 type samples are well preserved for two years.

(2) The observation says that the Tc confirmed with the Meissner effect signal is higher than (−) 100 ℃ and is about (−) 90℃.

(3) The observation suggests that the resistance of the HTS is very small and low at the room temperature and is sufficiently worthy of notice.

In conclusion, I would like to reexamine the results especially for (2), (3) items with the additional experiments in order to confirm these abnormal results and hope they will help me find information I am looking for and to encourage further work in high-Tc superconductivity.

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