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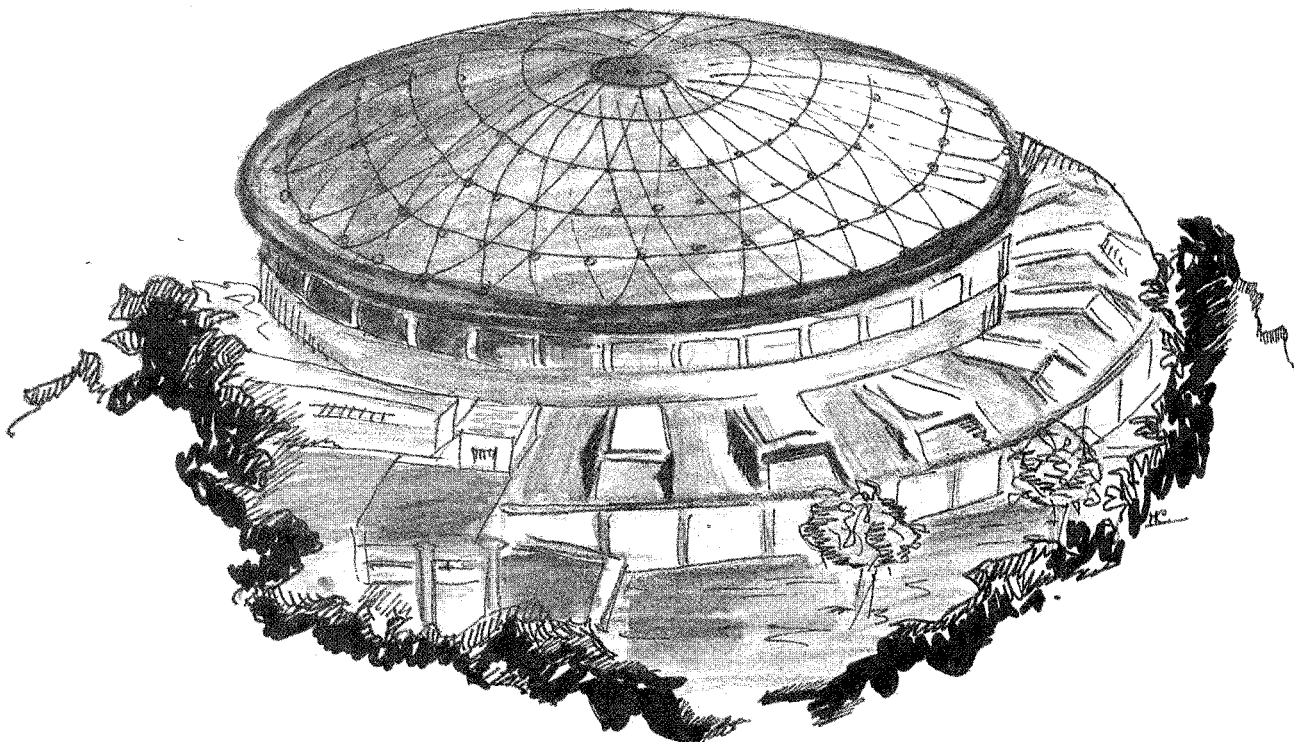
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MAXIMUM OF DIAMAGNETIC T_c AND MINIMUM OF ΔT_c**

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**OZONE ANNEALING OF YBCO SUPERCONDUCTORS: TOWARD THE
MAXIMUM OF DIAMAGNETIC T_c AND MINIMUM OF ΔT_c**

F. Celani, L. Liberatori, A. Saggese
INFN-Laboratori Nazionali di Frascati, P.O. Box 13, 00044 Frascati Italy

R. Messi
Dip. di Fisica Univ. di Roma II, Tor Vergata, 00173 Roma Italy

S. Pace
Dip. di Fisica Univ. di Salerno, 84100 Salerno Italy

N. Sparvieri
Selenia SpA, Direzione Ricerche, 00131 Roma Italy

ABSTRACT

A.C. low frequency susceptibility measurements, using the "inductance variation" method, have been performed on sintered YBCO pellets fabricated using a new process. This process is based on a modified citrate pyrolysis method and on the use of ozone in all the thermal treatments. The diamagnetic behaviour of this material have been studied as a function of the temperature changing both the amplitude of the a.c. magnetic field (0.2, 2, 8 Gauss) and the test frequency (120, 1K, 10K Hertz). At 0.2 Gauss the width (10%-90%) of the diamagnetic transition of the ozone samples is as low as 2K with a diamagnetic T_c of 98K. This width value obviously enlarges with the increase of the applied field: at 2 Gauss, with almost the same T_c , ΔT_c increases up to 6K. The behaviour at 8 Gauss clearly shows the contributions to the diamagnetic signal due both to the intergrain J_j coupling and to the isolated grains. The ozone annealed samples are compared with both oxygen annealed samples and samples made following the conventional calcination - refiring procedure: the last two show larger transition widths and a lower stability against water.

KEYWORDS

Superconductivity; High T_c ; YBCO; Ozone; A.C. Susceptibility;

INTRODUCTION

After the discovery of superconducting oxides (Bednorz *et al.* 1986), a race toward the materials characterization and the highest critical temperature T_c arose (Hor *et al.* 1987).

Due to the preparation easiness of sintered samples, showing the correct transition temperature by resistivity measurements, the experimental works on sintered pellets conducted sometimes to unsettled results. Indeed, it is obvious that the existence of some superconducting path with the correct critical temperature, checked by resistivity transition, does not insure the correct stoichiometry of the most volume of the sample and does not allow the detection of spurious phases. It is well known that every sintered sample shows a low critical current density due to the presence of spurious material on the grain surfaces. For instance, these surface problems lead to bad tunnel measurements. In the same way, any "surface" measurement on sintered pellets should be done with a lot of care to be sure that the material under measurement is actually superconducting. In order to avoid these problems, many efforts are spent for fabricate and characterize thin films and single crystals. In any case troubles for making large crystals and very good thin films still lead to interest in good quality sintered samples for both basic research and technological applications. For these reasons we have developed a new fabrication process of $Y_1Ba_2Cu_3O_{7-\delta}$ based both on a modified citrate pyrolysis method and on the use of an ozone enriched oxygen atmosphere (Celani *et al.* 1988a,b,c). The samples show both good mechanical and diamagnetic properties (Celani *et al.* 1988d,e) and the presence of a preferential texture of microcrystals (Celani *et al.* 1988b).

The optimization of the fabrication process needs the characterization of many samples, so that it is necessary a simple investigation method, able to determinate the pellets goodness. In spite of the simplicity the method requires accuracy, repeatability and has to be easy to use. We believe that the a.c. susceptibility measurements, using the inductance variation method as function of frequency, temperature and amplitude of the oscillating magnetic field is a simple and powerful method for a first characterization of the fabricated samples.

In this paper the main steps of the fabrication process together with the measurements apparatus are described. After we report measurements of superconducting diamagnetic transitions and discuss the role of screening current and of intergrain Josephson junctions. Comments and conclusions close the paper.

FABRICATION AND MEASUREMENT APPARATUS

Most of YBCO fabrication methods use the calcination processes, where, starting from powders (oxides, carbonates, etc.), the homogeneous mixing of Y,Ba,Cu in the correct stoichiometry is obtained only mechanically and by thermal diffusion. In different methods a

more intimate mixing is obtained using solutions.

Our fabrication process modifies the usual pyrolytic method, well known in the past, and recently applied to ceramics superconductors (Flokstra *et al.* 1987). Since the YBCO features are strongly dependent on the oxygen stoichiometry, to reach a complete and homogeneous oxidation of the compound, we use in all thermal treatments an oxygen atmosphere enriched with ozone which shows a very strong oxidation power.

The YBCO preparation starts from copper and yttrium oxides and from barium carbonate. After powder grinding, the addition of nitric acid transforms these powders into three "nitrate solutions" with some excess of nitric acid. The solutions are mixed together and the addition of citric acid forms metallorganic compounds avoiding the barium precipitation. The subsequent addition of NH_4OH drives the pH to the value of about 6.8. After the warming-up of this liquid the pyrolytic reaction starts. This reaction is exothermic and generates flames.

The final product is a fine black powder with granulometry of about 50 - 100 nm. The powder is then annealed at 950C into an alumina crucible in presence of 100 l/h flux of oxygen with roughly 1% ozone. After 12 hours the furnace is slowly cooled down to room temperature with a cooling rate of about 50 C/h. The compound obtained just after the first thermal cycle is almost completely superconducting as proved by later described diamagnetic measurements. The powder is ground, filtered, pressed and annealed again to obtain sintered samples of desired shapes. Usually cylindrical samples with diameter of ~20 mm and thickness ranging from 2 up to 7 mm are obtained.

All these samples have been characterized by using the home made equipment of Fig. 1. The insert is made of a PVC sample holder with a notch, where a silicon diode thermometer (DT470-13 Lake Shore) in good thermal contact with the pellet is located. The thermometer and the sample are almost thermally insulated from the external world. Coaxial to the sample, as shown in the insert of Fig.1, there is a coil made of about 200 turns of copper wire, whose inductance (~1mH) is measured as function of the temperature. This insert is dipped into a dewar initially cooled at 77K by a small amount of liquid nitrogen. The thermal leaks of the dewar determines a slow thermal drift of the insert (about 1K/min) toward room temperature. The silicon diode and the coil are connected respectively to a temperature controller (DRC-91C Lake Shore) and to a LCR meter (HP4262A Hewlett Packard).

The LCR meter can work only at three frequencies and, in order to maximize the resolution, in the autorange mode it works at fixed amplitudes of the a.c sinusoidal field. These amplitudes has been measured by a Hall probe and for 120Hz, 1KHz, 10KHz, are respectively equal to 8G, 2G, 0.2G. To overcome these constraints sometime a lock-in amplifier and an a.c. current generator have been used. As shown in Fig.1, the complete measuring apparatus is controlled by a personal computer through the HP-IB bus.

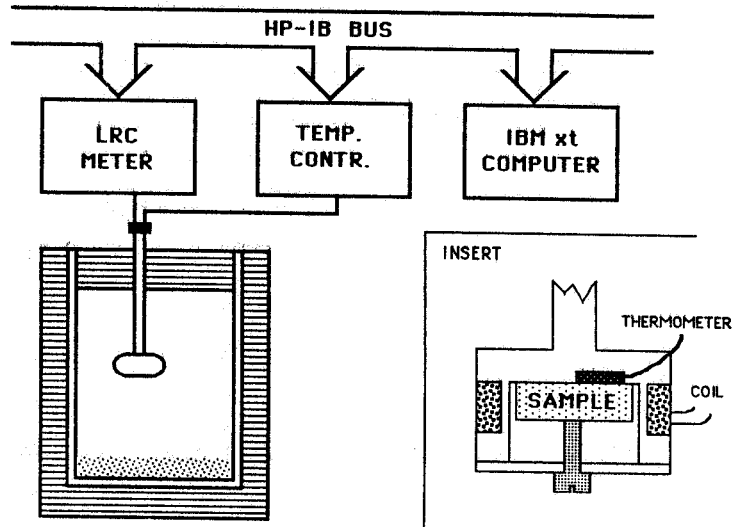


FIG. 1 - Experimental Set-Up for measuring the a.c. diamagnetic characteristic vs. temperature. The insert shows the sample holder with the pick-up coil and the thermometer.

SAMPLES CHARACTERIZATION

Below the critical temperature the superconducting shielding current of the pellet reduces the magnetic field inside the coil and leads to an inductance reduction. Because the pellets will never fill completely the inner volume of the measuring coil, due to geometrical factors, some linked flux exists. In order to detect the magnetic flux variation induced only by the samples, we define the inductance variation $\Delta L_S(T)$ as follow:

$$\Delta L_S(T) = L_V(T) - L_S(T) \quad (1)$$

where $L_S(T)$ is the inductance measured with the sample into the holder and $L_V(T)$ is the inductance measured with the sample holder empty. In this way also the stray flux is canceled out. In order to compare $\Delta L_S(T)$ with the complete shielding signal generated by an ideal superconductor, the apparatus has been calibrated by measuring at 4.2K several cylindrical lead samples having different thicknesses and diameters. The obtained reference signal ΔL_T have been interpolated in order to obtain the ideal signal as a function of the dimensions of cylindrical samples. $\Delta L_S(T)$ is then compared with the signal corresponding to an identical dimension lead sample by the ratio $\Delta L\%(T)$:

$$\Delta L\%(T) = \frac{\Delta L_S(T)}{\Delta L_T} 100 \quad (2)$$

The method has been tested by a high quality bulk niobium cylinder, obtaining the 100% expulsion percentage within the experimental accuracy.

The detailed temperature dependence of $\Delta L\%(T)$ for YBCO pellets has been performed in the temperature range 77-300K; further measurements were made at 4.2K. All measurements have been repeated at different values of frequency with the corresponding different amplitudes of the a.c. applied magnetic field.

In order to prove the effectiveness of the ozone during the sample preparation, a series of pellets have been made following the same fabrication process respectively with or without the use of ozone during all thermal treatments. Fig. 2 reports a series of curves obtained for different measuring conditions.

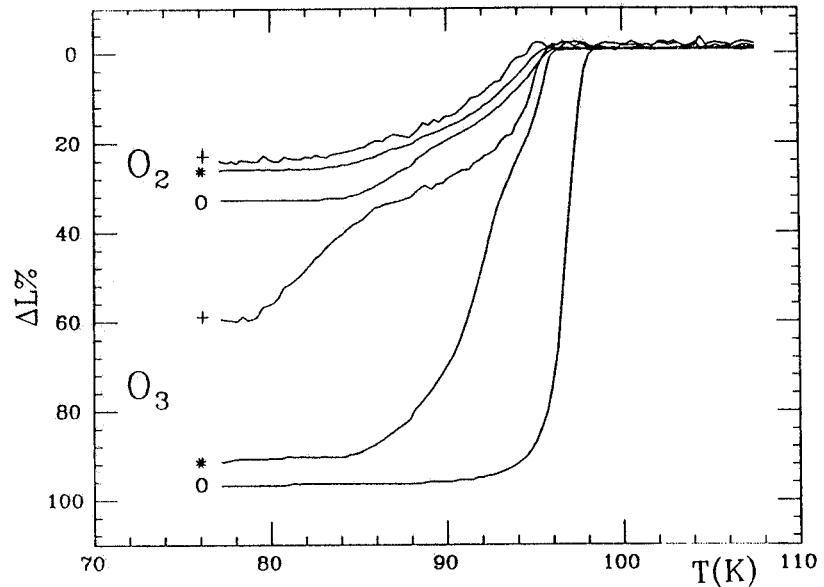


FIG. 2 - Inductance variation $\Delta L\%$ at different conditions for samples annealed in oxygen and ozone atmosphere. (+ freq. 120Hz, a.c. field 8 Gauss; * freq. 1KHz, a.c. field 2 Gauss; o freq. 10KHz, a.c. field 0.2 Gauss).

Measured samples were stored for more than six months using only small closed plastic boxes and were cycled many times between room and liquid nitrogen temperature without any care against water and moisture. The difference between ozone and oxygen is evident. The ozone transition curves are sharper, and reach the complete shielding value few degrees below the transition temperature. The curves enlarge only for a.c. magnetic fields of the order of tenth of Gauss. Indeed at 0.2 Gauss the diamagnetic superconducting transition width is only $\sim 2\text{K}$, while it becomes $\sim 7\text{K}$ and $\sim 16\text{K}$ respectively for a.c. magnetic field of 2 and 8 Gauss. Otherwise, in this temperature range close to the transition temperature and in the presence of the same a.c. magnetic fields, the oxygen made samples show a smaller inductance variation and a broad transition for all values of the a.c. applied magnetic field.

A.c. susceptibility measurements are sensitive both to superconducting shielding currents and to eddy currents induced into spurious normal conducting regions which may be present inside the material. Since the eddy currents are frequency dependent, it has been suggested (McCallum *et al.* 1982) that the dependence of the a.c. susceptibility on frequency is a good method to detect the presence of normal conducting regions. However someone in the literature reports different explanations of this frequency dependence.

Due to the use of the LCR meter the amplitude and the frequency are not independent. In our measurements, as reported by Celani (Celani *et al.*, 1988d), for good samples the amplitude dependence is dominant over the frequency dependence, so that in this paper only the main contribution is analyzed.

The interpretation of inductive transitions, performed with quite large oscillating magnetic

fields on granular sintered superconductors, is complex, but a naive picture of the obtained data can be done. Sintered superconducting pellets behave as an ensemble of weakly connected superconducting regions. The mean coupling strength decreases with the magnetic field and, due to thermal fluctuations, goes to zero for a critical field H_{c_j} dependent on the fabrication method. In any case this critical field goes to zero near the transition temperature. Close to the superconducting transition onset, since any measuring field is higher than H_{c_j} , the sample can be considered as an ensemble of disjoint grains. Decreasing the temperature the links between superconducting grains become stronger until H_{c_j} exceeds the measuring field and a macroscopic Josephson current can flow through grains and generates the shielding effect of the whole sample. In other words the magnetic field interferes with the intergrain Josephson junctions destroying the weaker couplings, so that measurements with different magnetic fields give information on the intergrain couplings strength.

Other effects can generate a broad transition such as:

- a) the existence of a distribution of the transition temperature due to a bad sample quality,
- b) the presence of small values of effective lower critical field induced by the granular nature of the sample and by a large number of small impurity regions.

In Fig. 2 the measurements at low field on ozone samples show a behaviour like an ideal bulk superconductor with a $\Delta L\%(T)$ of about 100% just 4K below T_c . In the 0.2 G curve the grains and junctions transitions are indistinguishable. The curves at higher fields show a double transition due to the breaking of grain coupling.

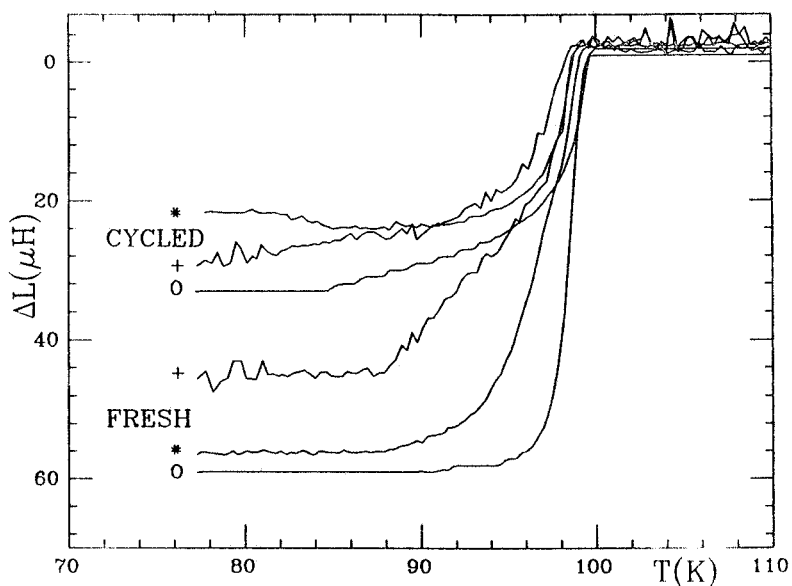
On the contrary, the oxygen sample have a broader diamagnetic transition, so that only at very low magnetic fields and at liquid helium temperature shows an almost complete shielding.

Moreover the onset of the transition temperature of ozone samples is about 2K higher than the corresponding oxygen one.

In order to test the sample stability the measurements were repeated several times with thermal cycling between room and liquid nitrogen temperature without cares against moisture and humidity. Beside samples made by pyrolysis, pellets made with different processes have been measured. The number of sample analyzed is not sufficient to judge any other fabrication method, however it is possible to demonstrate the weakness of low density samples made with the standard calcination - refiring procedure. Indeed Fig. 3 reports the measurements done as soon as the calcinated sample was fabricated, and after several thermal cycles. The irregular form of the measured pellet prevents the previously described volume normalization; for this reason Fig. 3 reports the inductance variation in μH .

Nevertheless the inductance variation shows a remarkable difference between the first measurements, when the material is fresh done, and the measurements after several thermal cycles. On the contrary, a large number of measurements, performed in the same environment on an old ozone sample does not show, up to now, noticeable degradation of the diamagnetic behaviour.

FIG. 3 - Inductance variation of a sample obtained by the conventional calcination- refining procedure. (+ freq. 120Hz, a.c. field 8 Gauss; * freq. 1KHz, a.c. field 2 Gauss; o freq. 10KHz, a.c. field 0.2 Gauss).
Fresh: sample as prepared.
Cycled: sample after several thermal cycles.



CONCLUSIONS

Samples fabricated with a modified pyrolytic process and respectively with the presence or absence of ozone in the oxygen atmosphere during thermal treatments have been analyzed by the temperature dependence of the a.c. susceptibility. In these measurements the inductance variation method was used as a simple method able to determinate the sample quality. Ozone samples have shown a complete shielding just below the transition temperature with "quite large" measuring magnetic field. On the contrary, oxygen samples have shown very broad diamagnetic transitions. Moreover, thermal cycling and water deteriorate low density samples fabricated by calcination processes. After many thermal cycles old ozone samples have diamagnetic transition better than calcinated samples after only few thermal cycles. In this way, both the goodness of the pyrolytic method and the improvement of the quality by using ozone enriched oxygen atmosphere has been confirmed. Our results have been recently corroborated (Berkeley *et al.* 1988) by the dramatic improvements in thin film deposition techniques determined by the presence of an ozone atmosphere.

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