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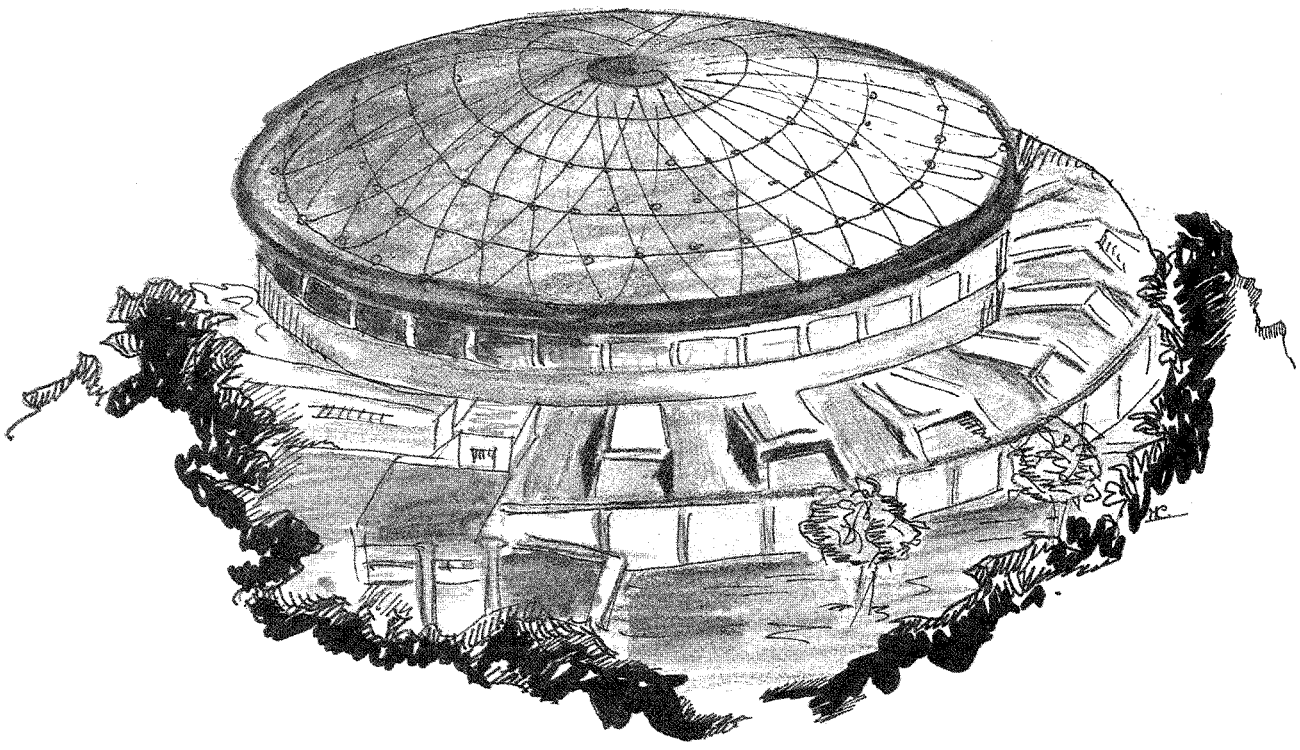

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PYROLYTIC CITRATE SYNTHESIS AND OZONE ANNEALING: TWO KEY STEPS TOWARD THE OPTIMIZATION OF SINTERED YBCO

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

W.I.F. David
Rutherford Appleton Lab. Chilton, Didcot, Oxon OX11 0QX U.K.

C. Giovannella, R. Messi, V. Merlo,
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

We describe a pyrolytic procedure that via a citrate synthesis allowed us to obtain very fine grained YBCO powders that, after a first furnace thermal treatment in ozone, results already to contain a large amount of superconducting microcrystals. A second identical thermal treatment gives a final product strongly textured, as shown by magnetic torque measurements. Complementary structural and diamagnetic measurements show the high quality of these sintered pellets. The role covered by both the pyrolytic preparation and the ozone annealing are discussed.

1. - INTRODUCTION

The technological applications of sintered YBCO are strongly frustrated by low critical currents and bad mechanical properties. The main problems are created by: a) the weak graincoupling, due to spurious materials among grains, b) the lowdensity of sintered pellets, and c) the large amount of defects, whose formation is often favored by spurious phases generated by a non homogeneous mixing before and during the reaction of the starting materials.

Indeed, in the last months, people have made a lot of efforts in trying to obtain an intimate reaction of the starting powders. To do this they used sophisticated milling machines to mix and grind the powders before and after the calcination processes. In different preparation methods the mixing of nitrate solutions is used.

In order to perform this task we introduced the modified pyrolysis method /1/ described in Sec. 2. This method allows us to obtain ultra fine and intimately reacted YBCO powders that, after ozone annealing, gives high density and grain oriented YBCO pellets. In Sec. 3 we summarize and discuss the results of the physical characterizations together with suggestions on the role of ozone annealing.

2. - PREPARATION METHOD

The preparation method used is an improvement of the pyrolysis citrate process which is well known in chemistry and used for the first time by J.Floxstra /2/ for the preparation of high Tc materials. The process starts with the formation of copper, yttrium and barium nitrates from copper and yttrium oxides and barium carbonate. The purity of the single powders is of the order of 99%. The fresh nitrates are produced adding 65% nitric acid. Of course, during this phase, a careful mixing is needed in order to avoid lump formation. The addition of citric acid leads to citrates and organometallic compounds avoiding the barium precipitation by means of Ba++ ions capture, obtained by the presence of carboxylic radicals. The pH value is adjusted by adding ammonia at 25% in order to obtain a pH value of 6.8 - 6.9.

It gives, among other things, ammonium nitrate which probably favores the subsequent combustion process. Care must be taken in order to avoid the salts precipitation. By heating the solution, at about 200C, the boiling mud shows a spontaneous combustion reaction. The final result of the combustion process is a very thin black powder with granulometry of the order of 100 nm. In Fig.1 and Fig.2 SEM pictures of the powders are shown. We retain that during the combustion process there is a quick transition from 200C to the temperature of a yellow-red flame, which can be roughly estimated to be of the order of 1500C, higher than the usual powder calcination processes. In any case the powders obtained by the pyrolytic combustion still contain some amount of spurious compounds and do not have a fully developed crystalline structure.

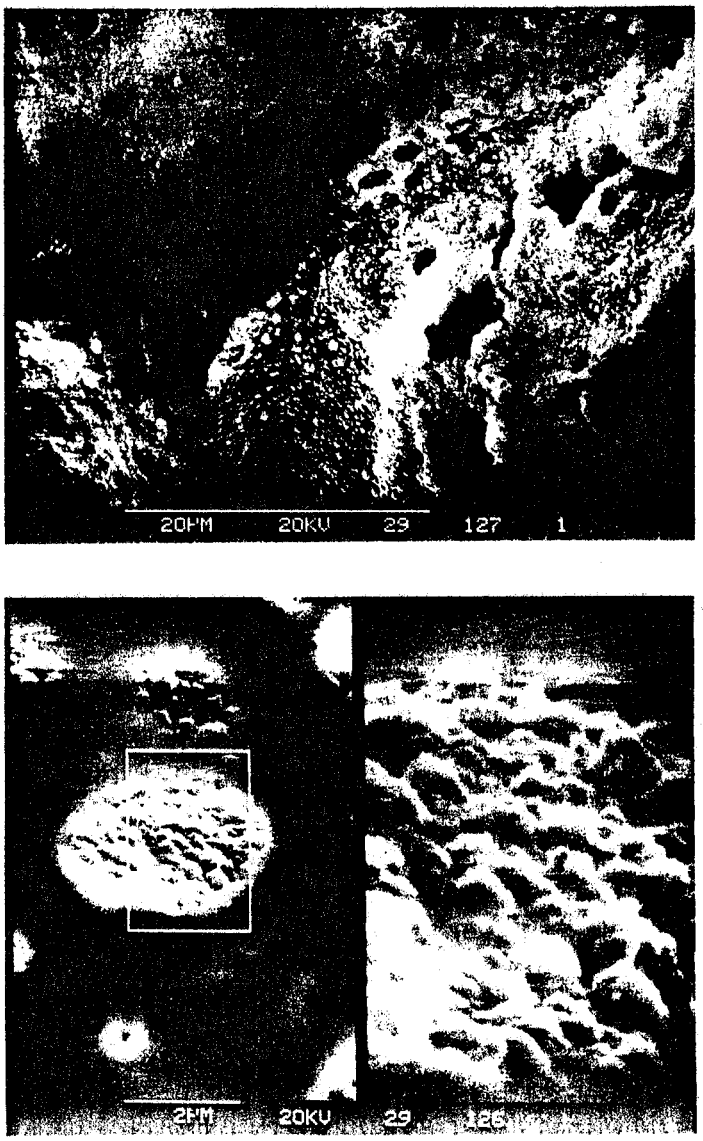

FIG. 1a,b - SEM pictures at different magnifications of YBCO powder after the pyrolysis.

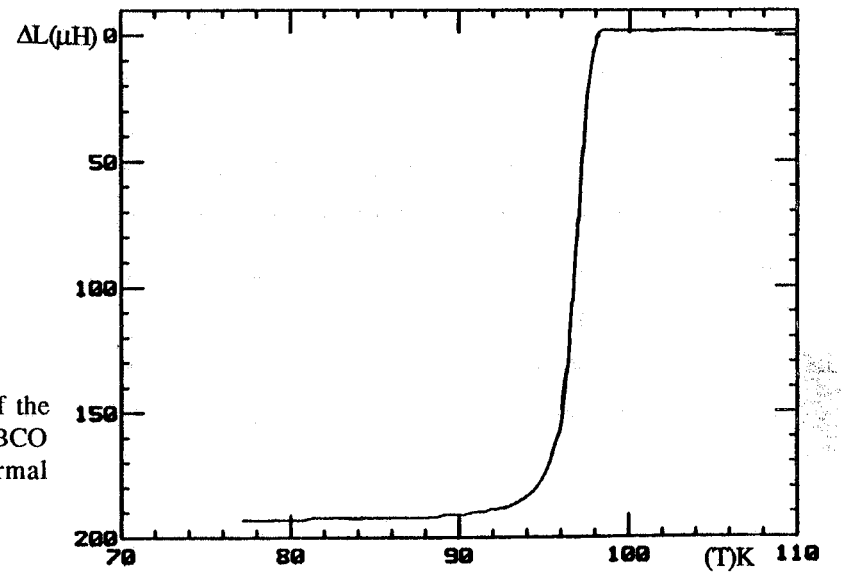

FIG. 2 - Temperature dependence of the susceptibility of a pressed pyrolytic YBCO powder after the first ozone thermal treatment.

After the reaction two identical thermal processes in an alumina crucible are performed: the rising time from 30C up to 960C is about 4 hours; after that a plateau of 10 hours and a slow cooling down to room temperature (lasting nearly 18 hours) follow. During both annealings we used a flow of about 100 l/h of dry oxygen enriched by the presence of ozone /3/. The ozone is produced by a home made electric discharger with an operating voltage of 20 kV and characterized by a fast rise time. The absorbed mean current is 10 mA and the percentage of produced ozone can be roughly estimated around 0.5%. It is not known however which fraction of ozone will arrive on the material as a function of the temperature.

In the first thermal process the fine grain structure of powders helps the ozone diffusion. After the first furnac treatment the powders are already superconducting. Indeed after grinding, filtering and pressing the powders at about 1 ton/cm^2 with a hydraulic press, the pellet exhibits a clear diamagnetic behaviour, as shown in Fig. 2 by the presence of a sharp fall of the susceptibility around 95K. Such data are obtained by an easy measurement of the inductance of a 200 turns coil surrounding a cylindrical pressed pellet with 20 mm diameter and height ranging from 2 up to 6 mm. In spite of this simple method, the measurement gives a significant quick test of the sample goodness. In Fig. 3 a SEM picture of the powders after the first furnace treatment in ozone atmosphere is shown: a large amount of microcrystals are visible.

After the second annealing the samples have the ceramic compactness with the density ranging from 5.5 to 5.9 g/cm^3 (this values are obtained measuring the pellets volume and weight).

Neutron diffraction measurements on a pellet have been performed at room temperature at the Rutherford Appleton Laboratory by using the High Resolution Powder Diffractometer.

In Fig.4 the neutron diffraction spectrum is shown. The good crystalline structure of the sample gave sharp diffraction peaks related to the orthorhombic structure with a high value of the ratio between the peaks amplitude and the background noise. The obtained lattice parameters are a=3.81Å, b=3.88Å, c=11.67Å. The oxygen stoichiometry results to be about 6.9.

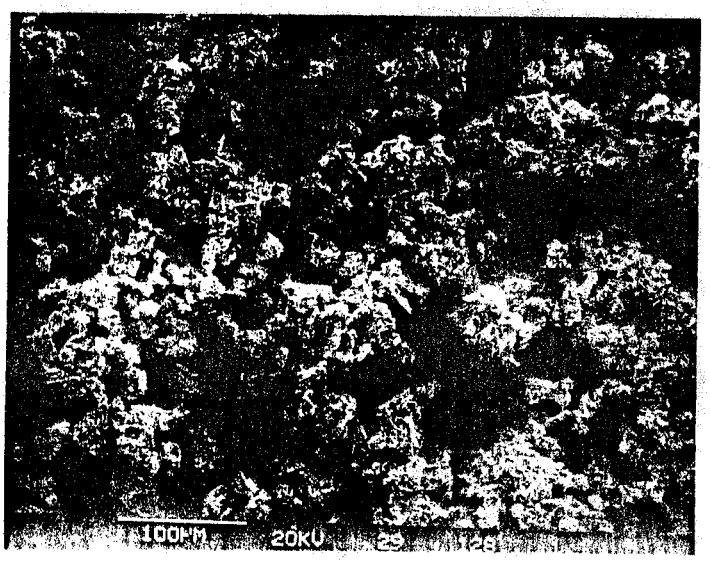

FIG. 3 - SEM picture of the pyrolytic YBCO powder after the first ozone thermal treatment. Some amount of microcrystals are visible.

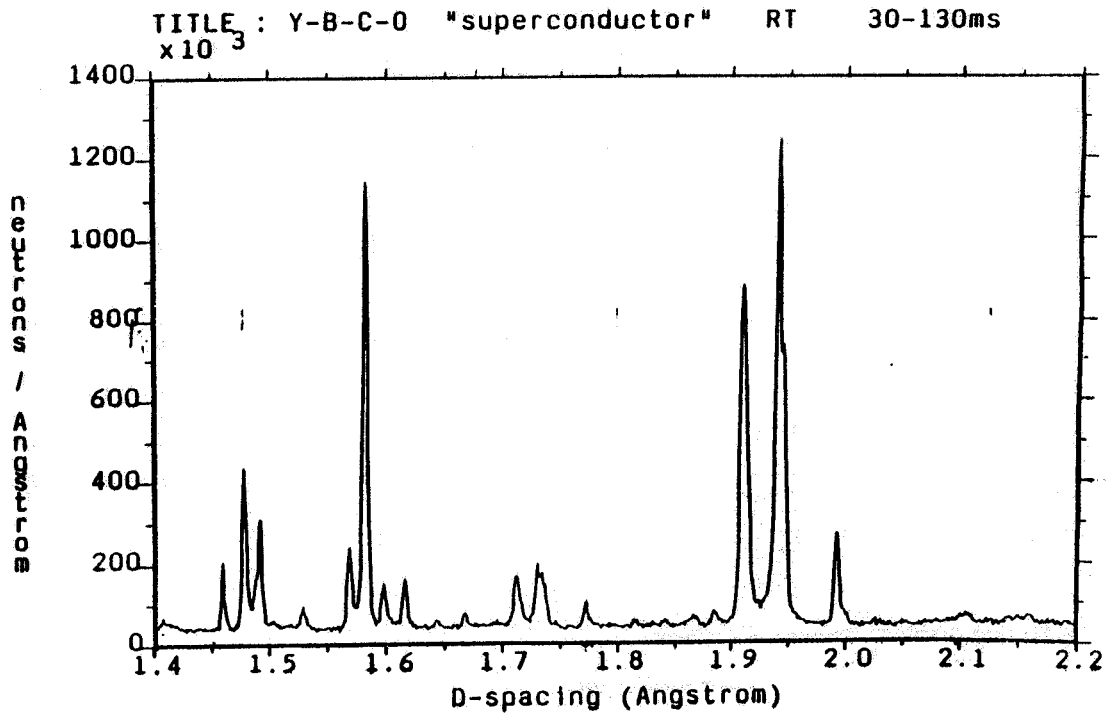

FIG. 4 - Neutron diffraction pattern of a sintered pellet; from a best fit procedure the lattice parameters are the following: a=3.81Å, b=3.88Å, c=11.67Å.

3. - CHARACTERIZATION

a) resistivity: resistivity measurements are performed with the usual four leads technique in the presence of the earth magnetic field. Fig. 5 shows a comparison between the resistive transition of an our high density (hd) and an usual low density (ld) sample.

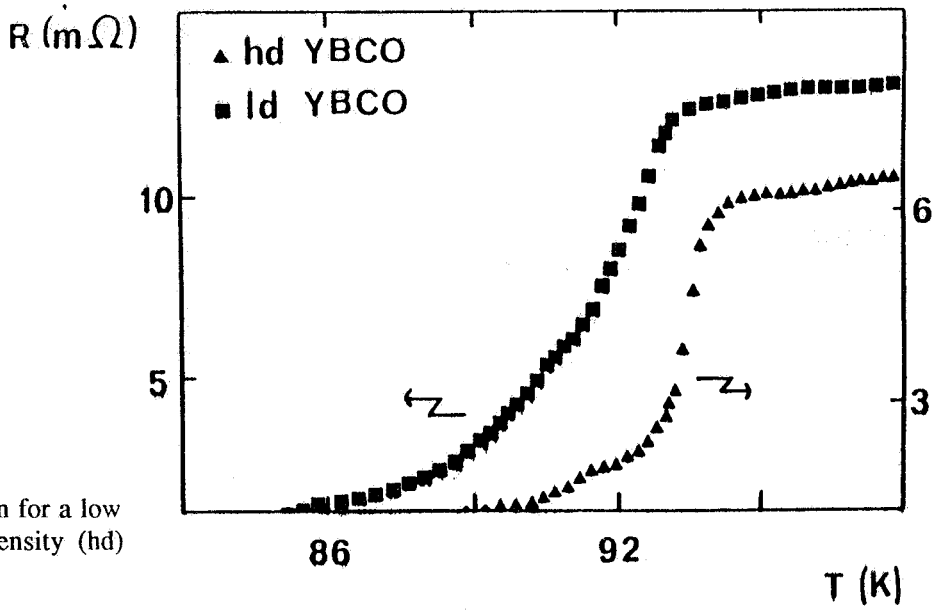

FIG. 5 - Resistive transition for a low density (ld) and a high density (hd) YBCO sample.

In these measurements a two step transition is often observed, where, after a first sharp fall, it follows a residual resistance which goes to zero slowly. This second contribution to the resistance

is linked to the presence of intergranular spurious material which leads to a weak coupling between grains (grain junctions). In our samples the high density of the final product suggests an intimate grain connectivity, indeed the residual contribution appears, in percentage, very low with respect to published data. Low quality samples shows both larger values of the residual contribution and a larger distribution of the individual grain transition temperature, which determines a complete mask of the double transition.

b) diamagnetic properties: in Fig. 6 we report the dependence of the d.c. susceptibility against the magnetic field at 4.2K both for hd and ld samples. The increasing of the magnetization with decreasing of the magnetic field is typical of single crystal behaviour. For our samples this behaviour could be related both to the absence of spurious local phases and compounds (which form pinning centers) and to the good intergrain coupling. The difference with usual sintered samples is evident. The coupling strength between junctions suggests the existence of more elevated critical currents and critical fields as proved by low field magnetization measurements /4/. Moreover, a.c. low frequency susceptibility measurements /5,6/ has been performed; the comparison between oxygen and ozone annealed samples showsfor the ozone samples both a large improvement of the diamagnetic signals and a better stability against water. Finally by these measurements the good intergrain coupling and the absence of spurious compounds is confirmed.

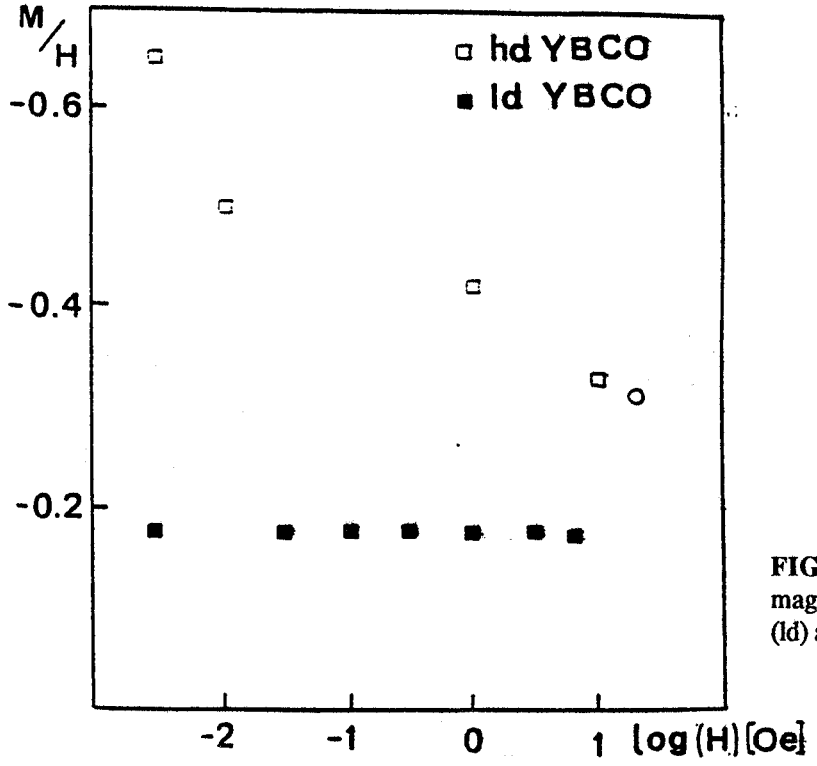

FIG. 6 - D.C. susceptibility vs. magnetic field at 4.2K for low density (ld) and high density (hd) YBCO.

c) torque measurements: the measurements of the magnetic torque/7/ show another important feature of the final product: the anisotropy. This behaviour is evident by the comparison between the torque signal obtained by measuring our samples and the signal obtained respectively with single crystals and usual sintered pellets /7/. This property is related to a preferential orientation of the large amount of microcrystals which are present in our pellets. Moreover, as shown in Fig. 7, from the

magnetic field dependence of the maximum of the rotational hysteresis /7/ some estimation of the critical field values (Hc1) along the direction a,b and c can be inferred. Such distinction cannot be performed in standard sintered samples because there exist a rather large distribution of the critical fields so that the two penetration steps are indistinguishable.

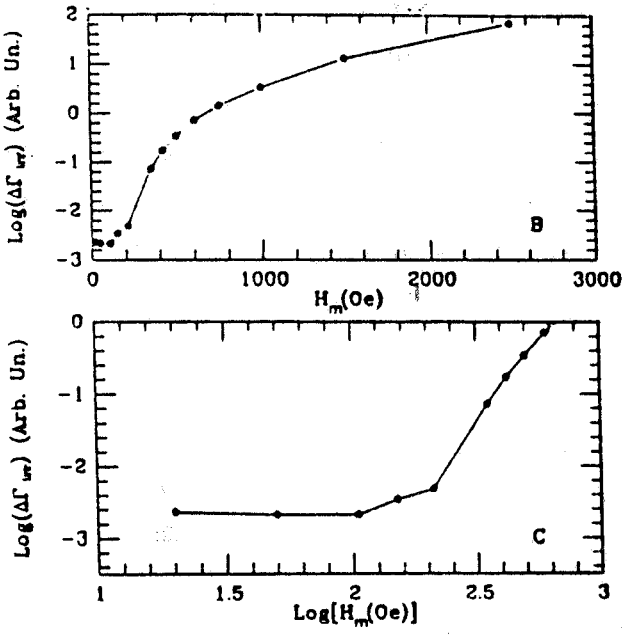

FIG. 7 - Dependence of the residual magnetization (pinned flux) $\Delta\Gamma_{i22}$ on the magnetic field. The lin - log (a), and the log - log (b) plots shows the existence of three regimes: a) a weak rotational hysteresis between 20 and 100 Oe, b) a first increase of the rotational hysteresis between 100 and 350 Oe, c) a strong hysteretic regime with a large penetration of the magnetic flux in the pellet.

4. - CONCLUSIONS

The method of pyrolysis of citrate for the YBCO preparation allows to obtain ultra fine powders that after ozone annealing produces single phase samples with extremely limited presence of defect as proved both by the high quality neutron diffraction pattern and from diamagnetic measurements.

The improved grain coupling cause good mechanical properties as well as better and stable diamagnetic behaviour. Moreover, the samples show strong anisotropic properties as shown by magnetic torque measurements. This behaviour can be ascribed to an oriented microcrystal structure. We retain that this effect is due to the combination of the homogeneous and fine grain structure of pyrolyzed YBCO and to the high reactivity of ozone which helps the growing of microcrystals during the thermal processes.

ACKNOWLEDGMENTS

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