TOPICS ON THE PREPARATION OF HTSC VIA SOLID STATE REACTION AND MELTING PROCESS

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The problems of the preparation of High Temperature Superconductors by sintering and melting are examined. Results of the thermal properties of the total substitution of Yttrium by a rare earth element are reported. The process of fabrication of HTSC after high temperature decomposition is indicated. The results of first characterisation are also reported.

Introduction

Up to date, at least three families of HTSC are known. All of them contain elements structurally related to perovskite.

The first is a series of materials based on the potassium-nickel fluoride structure (K_2NiF_4), doped with heavy alkaline earths, Strontium or Barium [1−3].

The second are the so-called 1-2-3 compounds that collect the $YBa_2Cu_3O_{7-x}$ and the rare earths substituted, where a Lanthanide substitutes Yttrium [4−6]. The oxygen content varies in a range from six to seven, formally corresponding [7, 8], respectively, to the unit cell with two divalent and one monovalent copper, or the unit cell where two divalent copper ions are together with a trivalent one. The structure is again related to the perovskite type and oxygen content is controlled by temperature and oxygen fugacity.

The third group of materials are complex oxides with alkaline earths, Ca, Ba and other ions as Bi or Tl [9, 10]. They form layered stuctures analogous to the previously known phases; their superconductivity is related to the number of planes sandwiched between perovskite-like layers, and their T_C is more than 120 K, the highest one so far discovered.

Other families [11] of superconductors can be considered; but their characteristics are less studied than the previous ones. For example, M. A. Subramanian *et al.* [12] report the existence of the new family of superconductors: $Pb_2Sr_2(Ca,Y)Cu_3O_{8+y}$, with $T_C = 77$ K. These compounds possess double Cu-O sheets separated by Y and Ca ions, analogous to the double sheets seen in $YBa_2Cu_3O_{7-x}$. In this paper the preparations and characterisation of $RBa_2Cu_3O_{7-x}$ (R = Y, Lanthanide) will be discussed.

The aim of this work was to obtain information about the thermodynamic stability of the highest T_C superconducting phases existing in the ternary systems $R_2O_3 - BaO_2 - CuO$, to investigate the appropriate condition to improved characteristics from superconducting samples also after the peritectic decomposition of the 1-2-3 phase [13, 14], and to study the possibility of improving the texture to obtain oriented grains to reach high critical currents (J_C).

Experimental and discussion

We have chosen to prepare the $RBa_2Cu_3O_{7-x}$ compounds by the solid state reaction based on the thermal decomposition of BaO_2 instead of $BaCO_3$ [15]. Good superconducting characteristics are obtained by heat treatments in air and with relatively short treatment time [16].

Highly pure substances must be obtained, and it is necessary to know the possible phases that can be grown during the process: therefore, the study of the phase diagram is essential, and especially the equilibria between the 1-2-3 phase and the nearest phases. In the following Fig. 1 a number of phases found in the literature are reported. But not all of them are really new phases.

Our group was able to confirm the compounds indicated with triangles (▲). The other ones indicated with squares (■) are either oxycarbonates (in fact they can be found only by the authors who use barium carbonate), or nominal compositions, or phases of which a structure is not reported.

The data indicated with circles (O) correspond to compositions that subsequently were found not to be single phases. Obviously it is possible that some phases exist which are not indicated or not yet discovered.

One could ask himself if the situation in other phase diagrams where Yttria is substituted by R_2O_3 is less complicated: even if the complete situation in the other phase diagrams is far from being fully studied, it can be anticipated that it is not so.
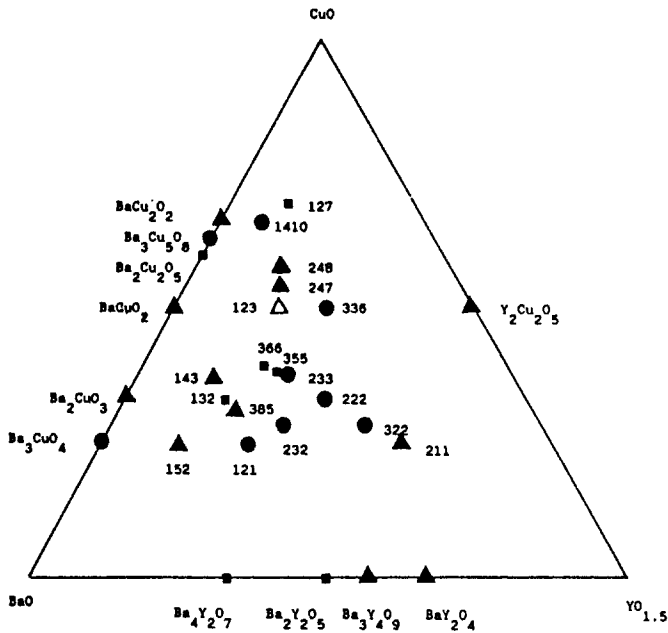
Fig. 1 Ternary system Y2O3-BaO-CuO showing primary phases suggested in the literature (Room Temp.). Inside the ternary diagram the composition of phases is given by numbers which represent the atomic ratio of the cations Y, Ba and Cu; e.g. 1410 is for $YBa_4Cu_{10}O_x$
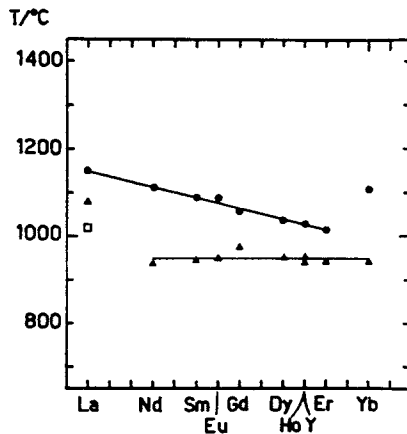
Fig. 2 DTA results of nearly single phase $RBa_2Cu_3O_{7-x}$. The maximum temperatures of the endothermic peaks of heating are reported

Here we refer only data on the thermal stability of the 1-2-3 phase with rare earth elements substituting Y. In Fig. 2 there are shown DTA results of nearly single phase $RBa_2Cu_3O_{7-x}$.

Unfortunately [17−19] all of them decompose peritectically (the thermal analysis is here limited to the decomposition temperature of the 1-2-3 phase). A regular behaviour presented by the thermal effects is evident. Two thermal effects are detectable above 900°: the first smaller thermal effect, present at a similar temperature in all the traces, was attributed by Mc-Callum et al., in their thermal study of $YBa_2Cu_3O_{7-x}$, [20] to the melting of $BaCuO_2$. This first thermal event above 900° is more or less at the same temperature, giving a further hint of an eutectic equilibrium in which $BaCuO_2$ could be involved also in the other phase diagrams. (It should be remembered that in preparing these oxides it was used BaO_2; so that the melting of $BaCO_3$, at about 930° is out of discussion). The second thermal event is due to the decomposition of the 1-2-3 phase. We notice that the trend of the peritectic decomposition temperatures (●) of different $RBa_2Cu_3O_{7-x}$ behaves regularly when plotted vs. the ionic radii of trivalent rare earths.

No information about tetragonal/orthorhombic (T/O) structural transition can generally be obtained from DTA curves. But it can be easily observed as a variation of oxygen activity by using an appropriate oxygen desorption system [21]. The oxygen stoichiometry is a determinant factor in the preparation of these superconductors. The dependence of T_C upon oxygen content is supposed to be known; collecting the results of Cava et al. [22] and Bukowski et al. [23] the courses are reported in Fig. 3. They claim to have had special care to the homogeneity of the sample vs. oxygen con-

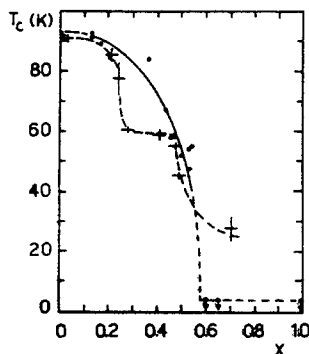Fig. 3 The critical temperature (T_C) of $YBa_2Cu_3O_{7-x}$ as a function of x. Data are taken from ref. [22] (+) and from ref. [23] (●). They are reported in the same scale taking into account the original shape

tent. As a matter fact, the two behaviours are not compatible to each other, and the true behaviour ought to be checked with accurate oxygen desorption and equilibrium experiments (eventually with the use of heat capacity measurements) [24].

1-2-3 samples partly superconducting are easy to prepare, but homogeneous and well defined single phase materials for evaluation of accurate physical parameters are difficult to obtain [25]. Characterisation of the samples follows the standard techniques reported elsewhere [26] of DTA, metallographic, microprobe and X-ray analysis and, when suitable, heat capacity [24] and resistivity analysis, then DC and AC susceptibility measurements [27]. But the most important parameter for applications is probably the J_C, the critical current that can be carried before the superconductivity is destroyed. A huge consequence has the morphology of the sample: the grain boundaries, some impurity, twinning are adverse factors [28, 29]. Fabrication methods using the molten oxide processing technique, which result in improved mechanical structure and properties over the sintering approach, can also be followed [30]. At 77 K both the density and the diamagnetism are influenced by the sintering temperature.

In Fig. 4a are reported the results of the densification experiments, obtained by sintering at different carefully controlled temperatures and procedures, both in air and in flowing oxygen, prereacted powders pressed into cylindrical pellets under 6 Kbar pressure [26].
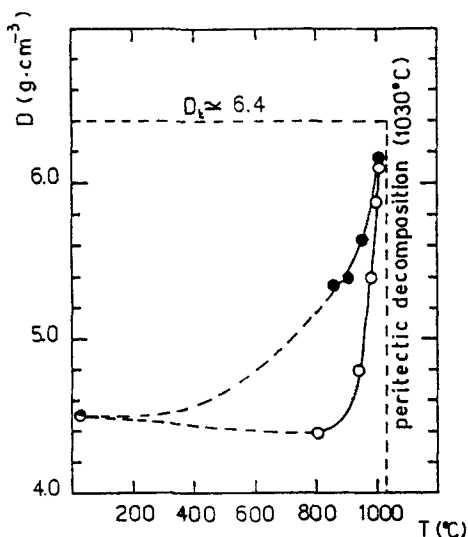

Fig. 4a Densification curves of YBa2Cu3O7-x. (●) D. of pellets sintered in flowing oxygen. (O) D. of pellets sintered in air

Note that the theoretical density is never reached without melting and this is probably due to the coarseness of the powders [26]. Moreover, the densification seems to proceed at different rates, depending on whether it is performed in pure oxygen or in air, although the highest value of densification is reached approximately at the same temperature of about $1000°$. Trying to sinter at higher temperatures, can lead to the appearance of a liquid phase that can be detected in DTA measurements. This liquid phase starts at about $990°$, in pure oxygen; although its presence can 'favourably' assist the densification, it causes that oxygen cannot be easily exchanged with the 1-2-3 phase. So, a subsequent longer annealing aimed at restoring the superconducting characteristics will be necessary.
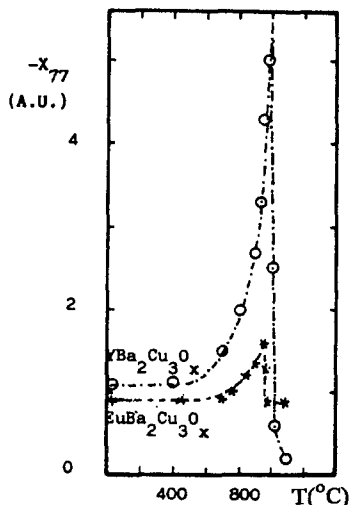

Fig. 4b Improvement of the DC diamagnetic susceptibility vs. the maximum sintering temperature, maintaining constant the other variables (time, atmosphere, etc.) for $YBa_2Cu_3O_{7-x}$ (O), and $EuBa_2Cu_3O_{7-x}$ (∗)

Figure 4b shows the evidence of a best sintering temperature in flowing oxygen for two different samples: $YBa_2Cu_3O_{7-x}$(O), $EuBa_2Cu_3O_{7-x}$ (∗). The sintering is performed at the same constant sintering time, oxygen pressure, heating and cooling rate. This does not mean that better samples cannot be obtained, but that the external conditions have to be changed.

The same behaviour exists also for the other R. E. substituted HTSC.

If however one would reach the goal of a good sintering (with eventual porosity included in grains, with sharp and thin grain boundaries), it is not

sufficient simply to increase the temperature, even if remaining at temperature lower than the peritectic decomposition temperature. For oversintered samples the diamagnetism is poor, C_p jump is not evident , the T_C remains undefined, and optimisation of oxygen uptake will be necessary.

The low critical current density in bulk polycrystalline sintered $RBa_2Cu_3O_{7-x}$ (R = Y, Ln) at 77 K and their unsatisfactory behaviour in magnetic field is one of the obstacles to significant progress in technical applications of the new HTSC.

Until today, the optimisation of the critical current J_C in sintered samples is a problem: in fact it drops very quickly even with weak magnetic fields due to the Josephson junction.

The techniques generally used to routinely characterise the occurrence of superconductivity are:

a) the resistivity drop; b) the low field a.c. susceptibility or diamagnetic shielding effect; c) the low field d.c. susceptibility, or flux expulsion [Meissner effect] when performed at H = const. and $dT/dt < 0$; d) the specific heat jump at T_C. Some of these techniques have some drawbacks that were pointed out by Junod et al. [24], for example the resistivity measurements and diamagnetic shielding effect [31] does not give quantitative results due to the fact that in sintered samples the powders can be connected through a percolative path, or grains could be covered by a superconducting coating that would lead to a zero resistance or full shielding effect in spite of a small volume fraction of superconductor.

Recovery after melting processes

In the melting process a previously homogeneous 1-2-3 phase is heated at temperature well above the temperature of peritectic decomposition, then it is cooled with various procedures to 1030°, where the peritectic reaction of formation of $YBa_2Cu_3O_{7-x}$ takes place.

Depending on the relative proportion of solids and liquid at the start of the reaction in a given alloy, the solid phases may be completely conserved or not. We are in the first case in principle, having started with the decomposition of the pure 1-2-3 phase.

But because the equilibrium cannot be thoroughly maintained and a certain amount of losses of material or wetting of the crucible is unavoidable, the peritactic reaction does not go usually to completion, and a slightly polyphasic sample can be obtained. Moreover, annealing must be performed to optimise the oxygen uptake, structural homogeneity and superconducting properties. Nor it seems to be profitable from this point of view to avoid

oxygen losses, to work at very high O_2 pressures. In fact it was observed by
J. Karpinski with E. Kaldis [32] that two more phases are stabilised (i.e. 1-2-
4, 1-2-3.5). and this will complicate further the phase equilibrium.

The problems that occur are: to obtain a good oxygen diffusion through
dense material, to avoid cracks in long pieces during the cooling down of
melted samples at the T/O structural transition.

The cooling down can be performed either in a homogeneous tempera-
ture field or in a suitable high thermal gradient of about $10-20 \, °C/cm$.
Thermal gradient results in texturing, i.e. alignment of the grains; details are
given elsewhere [14]. Local texturing is observed also in samples cooled in
the natural thermal gradient of the furnace ($1°C/cm$), as shown in Fig. 5, but
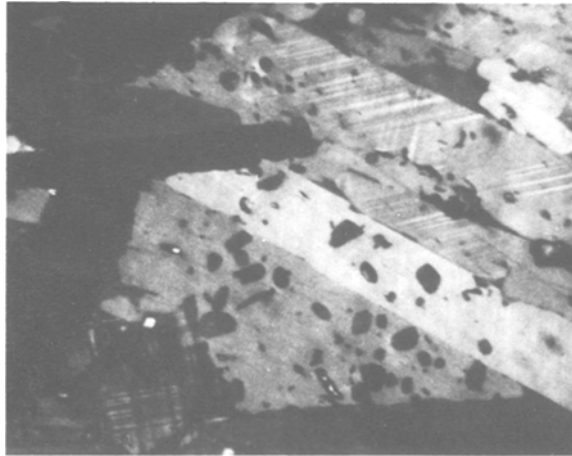a slightly polyphasic material is obtained and the connectivity of the grains

Fig. 5 Micrographic analysis of a partially textured sample after the high temperature
decomposition recovery process (etched with a dilute solution of acetic acid)

is poor. A different behaviour can be observed in highly textured samples.

Jin et al. [15] and Murakami et al. [16] have used another melting tech-
nique that proved itself suitable in reducing the problem of weak links and
in obtaining higher J_C in magnetic field.

The discussion that follows refers to samples only partially textured and
slightly polyphasic (<5%). However there is evidence is defected elongated
grains. The physical characterisation of the melt processed sample per-
formed by resistivity and a.c. susceptibility measurements [28] will be
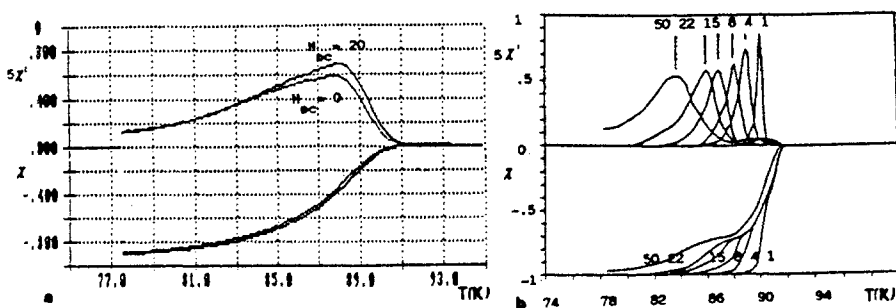reported elsewhere.

Fig. 6 Comparison between a melt processed sample (a) and a sintered one (b) in various H_{DC} Fields

Typical results obtained in melt processed samples are reported in Fig. 6 where the behaviour in magnetic field of melt processed and sintered samples are compared.

Notice that resistivity measurements, performed with the standard four wires techniques, can fail to confirm connectivity in textured samples formed by highly elongated crystals, when their dimensions reach the length of the four wires bridge, so that micrographic analysis is always necessary.

These preliminary results confirm the potentiality of melt processing procedure to overcome the stringent problem of J_C.

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Zusammenfassung — Probleme der Herstellung von Hochtemperatur-Supraleitern durch Sinter- und Schmelzvorgänge wurden untersucht.

Es werden Resultate der thermischen Auswirkungen der vollständigen Substitution von Yttrium durch Seltenerdelemente wiedergegeben. Der Prozess einer Herstellung von HT-Supraleitern nach thermischer Zersetzung im Bereich hoher Temperatur wird beschrieben, und es werden Resultate erster Charakterisierungen mitgeteilt.