Routes to obtain high performance, high $T_c$ superconducting bulk materials


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Dedicated to Professor Bernard Raveau on the occasion of his 60th Birthday

Abstract

This paper reviews our investigations for understanding the fundamental relations between physical properties, crystal chemistry, phases relation and processings on the compounds YBa$_2$Cu$_3$O$_{7-x}$ and Bi(Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+x}$. These two systems have in common the complexity of their crystal structure and multi-components chemistry which require challenging material processing for applications. In the YBaCuO system, horizontal bridgman and melting zone processes have demonstrated the possibility of obtaining high performances in this system, with different shaping. A high reproducibility with low material losses have been achieved with a top seeding melt texturing process. For BiSSCO based compounds, sol–gel and polymer matrix methods have been studied and developed with the achievement of promising critical current densities at 77 K.

Keywords: Superconductors, YBa$_2$Cu$_3$O$_{7-x}$; Bi(Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+x}$; Texturing process; Properties

1. Introduction

The discovery of high $T_c$ superconductors in the year 80 has open the way to numerous applications in the field of large current applications such as: Motors, generators, transformers, current leads, fault current limiters, transmission cables, energy storage (flywheel, SMES) magnetic bearings . . .

The benefits of the use of HTS materials is thanks to the absence of electric losses resulting from a joule effect, a large decrease in the refrigeration costs compared to the use of low $T_c$ materials, and also to an enhanced reliability.

However the development, on an industrial scale, of HTSC based devices has to overcome the problems linked to obtaining HTS materials having characteristics adapted to the given applications with a given geometry, and at a reasonable competitive cost.

Taking into account the bidimensional character of these materials, and their very low coherence length, good superconducting properties corresponding to a very large critical current and a large levitation force imply to texture the material in order to obtain large oriented monoliths and to avoid weak links. Besides the research and developments made by industry to produce wires and tapes (principally Bi$_{2223}$ and Bi$_{2212}$ based materials) via various routes have been proposed and developed by laboratories to fabricate single domain large pellets or bars (principally ReBaCuO based material).

This paper deals with the work performed at the Crismat laboratory in Caen by the ceramic team in order to improve the HTS materials performances and to correlate the superconducting properties and the domain size to the precursor characteristics, and to the texturing process.

The stability and the morphology of the Bismuth based materials being quite different than the ones of ReBaCuO based materials, the chemistry and the processes are quite different for the two families and are exposed in two separated parts.

2. YBaCuO system

2.1. Melt processing under thermal gradient

To overcome the $J_c$ limitations due to the weak link properties of the grain boundaries in sintered YBCO ceramics, the anisotropic growth of Y123 crystal favoured...
In the \(a,b\) direction there has been a tendency to develop texture formation processes. Weak link free current path in the texture direction is, thus, created due to the limited number of grain boundaries.

In order to obtain highly oriented samples Jin et al., in 1988 developed a melt process called Melt Textured growth (MTG) [1]. In this process, a sintered \(\text{YBaCuO}\) sample was melted and slowly cooled in a thermal gradient of 20 to 50°C/cm. The shape of the sample can be preserved thanks to the peritectic decomposition of the Y123 phase, above 1010°C in air.

\[
\text{YBa}_2\text{Cu}_3\text{O}_{7-x} \rightarrow \text{Y}_2\text{BaCuO}_3 + (\text{BaCuO}_2 + \text{CuO})\text{ liquid}
\]

for 1010°C < \(T < 1050°C\) (1)

The decomposition of the Y123 phase, controlled by the temperature and time at high temperatures, leads to a highly viscous melt, limiting, thus, the liquid losses.

The following slow cooling allowed the preferred orientation of the grain growth along the \(ab\) planes to take place and, thus, grains are aligned along this direction. The growth in the \(c\) direction is intrinsically three to five times lower than in the \(ab\) directions, thereby the final microstructure results in a stacking of 123 plates. The Y123 phase matrix includes Y211 particles, randomly distributed throughout the oriented grains, due to the liquid losses and to the incomplete peritectic recombination. The external thermal gradient imposed in this process provides a supplementary driving force which helps a planar Y123 growth front to take place and progress. Several observations have concluded that the growth of Y123 does not proceed through the classical peritectic reaction [2] which consists of the formation of a 123 envelope around individual Y211 particles. The investigators [3,4] proposed a growth mechanism based on the dissolution of 211 particles, which can be summarised as follow: Y123 phase nucleates in the melt where the composition is favorable and rapidly grows along the \((a,b)\) planes. The Y211 particles dissolve ahead the growth front to provide yttrium supply. Their dissolution creates a concentration gradient between 211/Liquid and Liquid/123 interfaces, which consist here in the intrinsic driving force for the diffusion of yttrium through the liquid phase to sustain the growth. Once the Y211 particles are entrapped by the growth front, they will not contribute to yttrium supply anymore. The continuous growth of Y123 requires a steady supply of yttrium which is only provided by the dissolution of Y211 particles in the liquid ahead of the advancing front. Since Y is only slightly soluble in the liquid [5] (about 2 mol.%) it is likely that its rate of transport to the interface will be the limiting factor of the growth.

The typical microstructure consists in large plate shaped 123 grains, occasionally including secondary phases. The developments of the melt processings of YBCO have revealed the importance of the processing conditions on the Y123 grain growth. This means that the precursor density (sintered or pressed), the temperature and time for the peritectic decomposition, the cooling rate or the moving rate, the external thermal gradient submitted to the sample are all important parameters to precisely know and control.

2.1.1. Horizontal Bridgman melt processing

We present here our investigations and results developed at the CRISMAT laboratory with the horizontal Bridgman melt processing techniques [6]. In this method, the whole sample, lying on a support, is decomposed above the peritectic temperature (typically 1150°C) and recrystallized by slow cooling of the furnace at 1°C/h in a thermal gradient of 10 to 25°C/cm. Theoretical studies by Cima et al. [7,8] have shown that a planar growth front and, thus, a continuous growth can be obtained with a compromise between the ratio \(G\) over \(R\) [\(G\) thermal gradient and \(R\) the processing rate] and the product \((G \times R)\) (expressed in \(^\circ\)C/h) representing the interfacial recrystallization rate which will determine the grain size, this latter varying inversely to the product \((G \times R)\). Enhanced domain size have been obtained from these considerations with the horizontal Bridgman method and single domains of centimeter size have been produced with a typical microstructure shown in Fig. 1. However, the necessary presence of a support below the sample provides reactivity, nucleation sites and unexpected radial gradients, making the formation of a large single domain difficult, in a reproducible manner. In this regard, the use of Y211 sintered bars [9] has been found to be one of the best candidate for Y123 support. Their similar components avoid pollution phenomena and their relatively close thermal expansion coefficients prevent crack formation in Y123, initiated by the contact between the sample and the support.

While reported \(J_c\) values of melt processed YBCO superconductors have already surpassed the lower limits for the practical applications, \(J_c\) enhancement above \(10^4\) A/cm\(^2\) and less severe degradation in high fields at 77 K are still required for better performances and an improved safety margin.

Transport \(J_c\) values of the MTG samples obtained by Jin et al. in 1988 exceeded \(10^4\) A/cm\(^2\) in zero field, at liquid nitrogen temperature, 77 K. This result indicated that grain alignment may have extensively reduced the weak links and lead to a great material improvement. However \(J_c\) values are below \(4000\) A/cm\(^2\) under 1 T applied magnetic field, at 77 K, which are still very low for practical applications.

The Y211 inclusions, like several other type of defects such as twin boundaries, dislocations and stacking faults have been considered as possible flux pinning centres; thus, the introduction of effective pinning centres in the microstructure has been and remains the constant guide for the obtaining of high superconducting performances.

Fig. 2 shows the magnetic field dependence of \(J_c\) at 77 K for three samples with different Y211 contents. In
Fig. 1. Typical microstructure of an horizontal Bridgman melt processed Y123 sample, observed by SEM. Fracture surface exhibiting the layered (a,b) planes. Polished surface with the Y123 superconducting matrix and the Y211 bright secondary phases inclusions.

horizontal bridgman melt textured samples, \( J_c \) values can be significantly enhanced between 0 and 1 T by increasing the Y211 content. This result supports the idea that Y211 inclusions are effective in flux pinning. Varying the concentration and sizes of the Y211 added to the Y123 powder precursor, Murakami et al. have shown that \( J_c \) at 77 K and under 1 T for various ratio volume fractions of Y211 over inclusion size, displays the direct proportionality between these two variables. This confirm the efficiency of controlling the microstructure of melt textured samples especially for what concerns the content, distribution and size of the Y211 secondary phase. We have tried to correlate the microstructure and the superconducting properties in melt processed YBCO through TEM and HREM studies [10]. Interfacial pinning between the superconducting matrix and the normal inclusions undoubtedly originates the properties enhancement, but other indirect effects have been also suggested, such as the increase of the dislocation density in the vicinity of the Y211 particles [11] or the modification of the twin structure and density [12,13]. These considerations are still under debate and investigations, to determine the most effective contribution of the Y211 particles in the pinning properties under low and high magnetic field.

As a further improvement, realizing the need for small Y211 particle sizes and their homogeneous distribution in the melt, we have studied the effects of dopants such as platinum, cerium and tin on the Y123 growth conditions. The dopants actions are not yet clearly understood, but their benefit is essentially attributed to their action on the Y211 particles by modification of the molten state (Y211 morphology and dissolution, interfacial energies and kinetics, viscosity of the melt) and modification of the Y123 growth rates; we have also observed a reduction of the grain growth anisotropy in doped samples, that means between the (a,b) planes and the \( c \) direction, leading to an improved microstructure and enlarged domain size. With the introduction of such dopants in the nominal composition some secondary phases are formed but the superconducting Y123 matrix might also incorporate these foreign elements. As a consequence the superconducting transition temperature might be affected. Fig. 3 shows that the \( T_c \) values might be slightly depressed to by 2 wt% cerium doping while 0.5 wt% platinum preserves a high \( T_c \) value, above 92.5 K for \( T_c \) onset; the combination of cerium and platinum gives an intermediate result with a the \( T_c \) onset at 92 K. In these three cases, the transition is similar and quite broad (about 3 K).

The effect of these dopants on the superconducting properties of MTG samples grown in a thermal gradient with the horizontal Bridgman method are illustrated in Fig. 4. Platinum is effective in maintaining the \( J_c \) values under magnetic fields up to 1 T, while cerium greatly increases
the $J_c$ values in self field and very low field. The combination of these two dopants (0.5 wt% CeO$_2$ and 0.5 wt% PtO$_2$) leads to very interesting $J_c$ values at 77 K, exceeding $6 \times 10^4$ A/cm$^2$ in self field and still $4.5 \times 10^4$ A/cm$^2$ under 1 T).

In conclusion, due to grain alignment in melt-textured Y123 slowly recrystallized in a thermal gradient, the critical currents densities $J_c$ obtained from magnetic or transport measurements with the current flowing in the highly superconductive $(a,b)$ planes, can reach 105 A/cm$^2$ at 77 K and zero field. Even though these $J_c$ values are relatively large and promising, a strong $J_c$ anisotropy is observed when the direction of the applied field is varied and these values are limited by depinning. Improvement in $J_c$ has been achieved by introducing additional flux pinning centres to the microstructure with an accurate control of the latter. The Bridgman melt texturing methods have been developed to accomplish this task, especially with Y211 and dopants addition which results in an increasing number of small Y211 precipitates of less than 2 microns size and leads to $J_c$ values now close to the requirements.

However, this method does not allow the whole sample to be submitted to the same thermal treatment. The growth front progress, from one extremity of the sample to the other, imposes a different holding time above the recrystallization temperature all along the sample. This might leads to variation of the composition of the melt, of the liquid losses and of the Y211 inclusions size and distribution along the sample.

This study has also shown evidence of the close relation the $J_c$ values in self field and very low field. The combination of these two dopants (0.5 wt% CeO$_2$ and 0.5 wt% PtO$_2$) leads to very interesting $J_c$ values at 77 K, exceeding $6 \times 10^4$ A/cm$^2$ in self field and still $4.5 \times 10^4$ A/cm$^2$ under 1 T).

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This study has also shown evidence of the close relation between precursor, composition and thermal process which cannot be independently considered in the search for an optimized and reproducible way of production of large quantities—high performances YBCO superconductors.

2.1.2. Melting zone process

In the previous section the classical Bridgman method is described in which the sample, having a paralleleped shape, is slowly translated across a tubular horizontal furnace which imposes a partial sample melting zone. The sample displacement allows, thus, the formation of a recrystallization zone conductive to obtaining a well textured sample. However, the sample in contact with the Al$_2$O$_3$ or Y211 support can be contaminated or submitted to undesirable gradients during the thermal treatment.

The method developed is to replace the horizontal geometry by a vertical configuration. The principle is to attach the sample (bar or paralleleped) by its upper part and to translate it from the bottom to the top or inversely. Even if the contamination is now avoided, since the sample is totally suspended, the new difficulty is to stabilize the lower sample part which is sustained by the liquid phase resulting from the partial melting zone. In practice, if the sample length suspended below the liquid phase is not too long, the high liquid viscosity allows one to mechanically sustain the suspended part. However, a reduction in the sample section, after the texturing treatment, is observed due to the sample elongation directly linked with its weight. In the Crismat laboratory, we have developed such techniques. Here, we present results we obtained when a Y123 material was textured using two different heating furnaces: A classical and a microwave furnace. If the conventional vertical furnace is currently used for texturing Y123 bar [14], the Crismat laboratory is the pioneer concerning the development of the microwave furnace for texturing Y123 bars.

In a conventional furnace, the formation of a single-
domain Y123 bar is observed when the solidification speed is lower or close to 1 mm/h, which constitutes one of the process limitations. This is the reason why we have investigated the possibility of increasing this speed by using appropriate doping elements (SnO$_2$ or/and CeO$_2$) [15] and developing the microwave furnace which imposes a higher thermal gradient [16]. Indeed, Cima et al. [7] demonstrates how Y123 crystal growth can be enhanced when the applied thermal gradient in the vicinity of the growth front is high (higher than 150°C/cm). In addition, some experiments have been performed applying very high thermal gradients (>$10^8$C/cm) using methods as Laser Heating Floating Zone (LHFZ) or image furnace but, in these cases, due to the very high thermal gradient, liquid migration was observed leading to a process that was difficult to control [17]. Consequently, the microwave furnace, which imposes an intermediate gradient compared with theses latter processes, and the conventional furnace appear to be very interesting for texturing Y123 in good conditions.

Fig. 5 shows the two thermal profiles measured along the vertical axe using a type S thermocouple in the classical and in the microwave furnace. In these graphs, we can observe that the thermal gradient ($G$) is close to 60°C/cm in the case of the classical furnace and reaches 260°C/cm in the microwave one. It is also observed that the maximum temperature is the same for both processes (about 1060°C).

Several bars were melt processed at different speed using the two processes and were compared in terms of microstructures and transport properties ($J_c$). The $J_c$ was measured using the four points method at 77 K by injecting a pulse current (see Fig. 6). Indeed, due to the bar sample diameter (about 4 mm), the critical current achieves several thousand amperes and thus, these high current values can be achieved only with pulse current.

The maximum speed which allows the formation of a single-domain has been determined to be close to 2 mm/h for both processes. Consequently, the applied thermal gradient does not appears to be a crucial parameter which permits an increase in the growth rate. However, polarised optical microscopy observation of melt processed samples textured using the two kinds of furnaces, with a solidification speed higher than 2 mm/h, shows a fundamental difference (see Fig. 7). Radial grains boundaries are observed on samples melt processed under the lowest thermal gradient compared with the other samples which contain only axial grains boundaries. This observation can be interpreted by the fact that, even if the axial gradient ($G_a$) is large and leads to a continuous growth along the bar, the radial gradient ($G_{rad}$) is low for both processes and new nucleation occurs in this particular direction, leading to the formation of several domains. Transport properties are correlated with the microstructure as can be seen in Table 1. When the solidification speed is lower than 1.9 mm/h for both processes, the transport $J_c$ at 77 K achieves approximately 20 000 A/cm$^2$. This value is very high compared to the value of transport $J_c$ reported in the literature in spite of the disorientation of the $(ab)$ planes in our bar [18,19]. Generally, the $(ab)$ planes are 40/45° disoriented from the bar axe [20], which is naturally not the ideal orientation. When the solidification rate is close to or higher than the critical speed which determines whether or not a single-domain is obtained (1.9/2 mm/h), the $J_c$ decreases drastically in the case of sample melt processed in a classical furnace. On the contrary, sample melt processed using the microwave device and with the same solidification speed, exhibits very high $J_c$ (19 700 A/cm$^2$). This difference is also observed when the solidification speed imposed by the process is higher than 1.9 mm/h.
the \((ab)\) planes orientation and to introduce into the Y123 matrix nano-particle of element doping.

### 2.2. Isothermal texturing process: Top seeding melt texturing growth

As already mentioned, the geometry of the superconductor depends on the practical application it is devoted to. Applications regarding levitation, such as flywheel energy storage systems, contactless superconducting bearings or permanent superconducting magnets [22–27], require pellets with high levitation forces. The repulsive magnetic force \(F_L\) between a magnet and a superconducting material is proportional to the induced currents and to the size of the current loop \(d\) in the superconductor. Because of the anisotropic structure of \(\text{YBa}_2\text{Cu}_3\text{O}_7\) \((\text{Y123})\), the maximum force can, therefore, be reached with the \(c\) axis domains parallel to the pellet axis, i.e. with the induced current flowing in the \(ab\) planes, where critical current density \(J_c\) is the highest. In this configuration, \(F_L\) is proportional to \(J_c\) and \(d\). The top seeding melt texturing growth process has been developed in order to optimize this force [28–32]; the goal is to fabricate a large single domain, in order to have a large current loop, and well oriented with the \(c\) axis parallel to the pellet axis. \(\text{Y}_2\text{BaCuO}_5\) \((\text{Y211})\) and dopants are also added to increase \(J_c\) and, hence, \(F_L\).

At the CRISMAT laboratory, we have chosen to work in isothermal conditions. Indeed, it allows to texture batches of several samples at the same time. Moreover, the size of the domain is not limited by the size of the furnace, as it is often the case for texturing in gradient furnaces. In the first part of this Section, we will briefly present the top seeding melt texturing growth \((\text{TSMTG})\) process: The control of which is correlated with the absence of radial grain boundaries. On the contrary, samples melt processed under lower gradient have very low \(J_c\) in correlation with the presence of radial grains boundaries which limits considerably the current flow [21]. Consequently, microwave processing of textured Y123 material appears advantageous compared with classical method and is very promising for future applications such as the production of current leads or limiters. However, for still improving \(J_c\), studies are also in progress to control

Thus, the \(J_c\) of sample processed in the microwave cavity at 2.3 mm/h still exhibits high \(J_c\) of about 10 000 A/cm\(^2\), which is correlated with the absence of radial grain boundaries. On the contrary, samples melt processed under lower gradient have very low \(J_c\) in correlation with the presence of radial grains boundaries which limits considerably the current flow [21]. Consequently, microwave processing of textured Y123 material appears advantageous compared with classical method and is very promising for future applications such as the production of current leads or limiters. However, for still improving \(J_c\), studies are also in progress to control

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**Table 1**

Resume of transport \(J_c\) at 77 K versus the translation speed and the technique used

<table>
<thead>
<tr>
<th>Technique used</th>
<th>Translation speed (mm/h)</th>
<th>(J_c) (A/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Classical</td>
<td>1.3</td>
<td>19 600</td>
</tr>
<tr>
<td>Classical</td>
<td>1.9</td>
<td>4200</td>
</tr>
<tr>
<td>Classical</td>
<td>2.0</td>
<td>6300</td>
</tr>
<tr>
<td>Microwave</td>
<td>1.3</td>
<td>22 000</td>
</tr>
<tr>
<td>Microwave</td>
<td>1.9</td>
<td>19 700</td>
</tr>
<tr>
<td>Microwave</td>
<td>2.3</td>
<td>10 000</td>
</tr>
</tbody>
</table>
their decomposition temperature is only 30 to 60°C higher than the Y123 one. Melt textured SmBa$_2$Cu$_x$O$_{y-z}$ is commonly used as it is easier to obtain than NdBa$_2$Cu$_x$O$_{y-z}$ [31,32]. The maximum temperature of the texturing thermal cycle should then not overcome 1055°C. Small single domains of 2 to 4 mm$^2$ surface are cleaved parallel to the $ab$ planes and placed on the top surface of the Y123 pellet.

- The second step is the determination of the temperatures of heterogeneous nucleation from the seed and homogenous nucleation in the melt. In this temperature window, a domain can grow from the seed without being hindered by parasite random nucleated domains.

The temperature difference can be explained thermodynamically. Indeed, at a given temperature, the nucleation barrier is lower at the contact between the seed and the melt than in the melt. Consequently, the nucleation from the seed appears at a higher temperature than the nucleation in the melt. A series of quenches permits one to determine this nucleation window, which can vary from 6 to 10°C as a function of the composition [32–35].

- The last step is the measurement of the Y123 crystal growth rates along the $a$ (or $b$) and $c$ directions. They are calculated from the progress of the growth fronts inside the nucleation window. The processing cooling rate in the nucleation window is then adjusted to these velocities in order to grow the desired oriented domain.

This process leads to a good control of the orientation and of the growth of the Y123 domain. Fig. 8 shows a photograph of a TSMTG textured Y123 pellet. Nevertheless, to increase the levitation force, superconducting properties should also be enhanced. Different compounds are added to Y123 in order to optimize these properties.

Levitation forces being proportional to $J_c$, our work has focused on increasing the critical current density. Y211 fine inclusions are well known to enhance flux pinning under low fields. Hence, a Y211 excess is initially added to Y123 pellets. Moreover, the additional green phase limits the liquid loss during the high temperature stage and is a Y source for the Y123 recombination, dissolving near the Y123 growth fronts [36]. An excess of 25 to 40 mol% leads to the best superconducting properties. This corresponds to a textured material containing 20 vol% of Y211, i.e. 40 mol%, whatever the initial amount is [36].

As Y211 particles tend to coarsen on the Ba–Cu–O melt, different dopants are used to obtain a final Y211 of size smaller than 2–3 μm. Platinum was found to be very effective in this way by decreasing the interfacial energy between Y211 and the melt [29,33,37]. Fig. 9a illustrates the micron and sub-micron size Y211 distribution in melt textured Y123 doped with 0.5 wt% PtO$_2$. A small angle neutrons scattering was performed on a 2 cm diameter textured pellet and shows a $c$ axis spread of 4°. Growth rates of 0.5 mm/h in the $ab$ planes and 0.3 mm/h along $c$ were measured. Superconducting properties of Pt doped samples are given in Figs. 10 and 11. The superconducting transition occurs at 91.8 K with a transition width of 1 K. Critical current density reaches 50 kA/cm$^2$ under 0.2 T, 25 kA/cm$^2$ under 1 T and 15 kA/cm$^2$ under 2 T at 77 K. The levitation force of a 3 cm diameter pellet measured with a 3 cm diameter SmCo magnet is 55 N.

In spite of its beneficial effects, because platinum is very expensive, efforts have turned to find another dopant that would have the same influence on Y211 and that would be more attractive from a cost standpoint. In previous studies, we reported the texturing of 0.5 wt% CeO$_2$ doped Y123 [32]. Cerium inhibits the Y211 coarsening during the melting stage and leads to micron and sub-micron size Y211 inclusions as illustrated on Fig. 9b. A $c$ axis spread of approximately 3° was found by rocking curve, indicating a texture quality similar to the Pt doped samples.

Cerium increases the melt viscosity and, thus, reduces a little bit the growth rates of Y123 to 0.4 mm/h in the $ab$ planes and 0.25 mm/h in the $c$ direction. However, cerium entering the Y123 matrix, $T_c$ is decreased to 90.5 K with a transition width of 1.5 K as shown in Fig. 10. The $J_c$ curve is shown in Fig. 11. $J_c$ attains 60 kA/cm$^2$ under self-field, 20 kA/cm$^2$ under 1 T but falls to 5 kA/cm$^2$ under 2 T at 77 K. Levitation force measured on a 30 mm diameter pellet is 45 N, which is a little bit lower than the Pt doped sample.

In order to enhance growth rates and $J_c$ under field, tin was added to cerium doped mixture. Indeed, tin is known to diminish the melt viscosity and to improve pinning under field [34,35]. An addition of 0.25 wt% SmO$_2$ to the 0.5 wt% CeO$_2$ doped Y123 allows, without destroying the cerium beneficial effects, to reach growth rates of 1.5

![Fig. 8. Photograph of a 30 mm diameter TSMTG Y123 pellet.](image-url)
mm/h in the \( ab \) planes and 1.8 mm/h in the \( c \) direction. The microstructure is shown in Fig. 9c. The Y211 distribution is still very fine. Moreover, superconducting properties are greatly improved as can be seen on Figs. 10 and 11. Onset \( T_c \) recovers a value of 91.2 K with a transition width of 0.5 K and \( J_c \) rises up to 90 kA/cm\(^2\) under self-field, 50 kA/cm\(^2\) under 1 T and 25 kA/cm\(^2\) under 2 T, which are to our knowledge among the best values ever obtained for melt textured Y123. These improvements are believed to be due to sub-micron size inclusions containing Y, Ba, Cu, Ce, Sn, and O. Investigations are still in progress. The levitation force has not been measured yet but promises to be important regarding the above critical current obtained.

In conclusion, the isothermal TSMTG process gives a good control of the growth and of the orientation of a Y123 domain, while allowing to texture batches of several pellets in one run. Moreover, the addition of an excess of

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Fig. 9. (a) Microstructure of 0.5 wt% Pt doped Y123; (b) microstructure of 0.5 wt% Ce doped Y123; (c) microstructure of 0.5 wt% Ce + 0.25 wt% Sn doped Y123.
methods, because a small variation of the starting composition may result in various phase equilibria [38–42]. The solid-state reactions started with oxides and carbonates [43] and the carbonates remained up to 800°C and may lead to a non-equilibrium and chemically non-homogeneous condition for the powder. The better chemical homogeneity and activity of the sol–gel [44] and the polymer matrix methods [45], compared to that for the solid-state reaction, may result in a better kinetics of the (Bi, Pb)-2223 formation. After the calcination step, the powder is milled and pressed into pellets. These pellets are then sintered at temperatures from 825°C to 860°C and quenched after various time from 5 to 100 h. X-ray powder diffraction measurements show that the best evolution during sintering, of the 110 K phase weight fraction conversion rate, is obtained at 850°C for the three methods and Fig. 12 shows those evolutions for different soak times calculated on the basis of the intensity ratios of 2223 and 2212 XRD peaks respectively.

It is clearly shown that the solid-state route requires much more sintering time to form a high 2223 phase percentage than the solution process methods. The same observation has also been made for the 2212 formation rate, when comparing these three methods [46].

To calculate the activation energy $E_a$, the Avrami relation [47] was used, which gives information on the reaction order $n$ (Fig. 13):

$$C_{10}(t) = 1 - \exp(-K t^n) \quad \text{and} \quad K = K_0 \exp(-E_a/RT)$$

Our results are consistent with two different reaction orders at short and longer sintering times as observed by Grivel [48] and confirmed by Huang [49]. The classical synthesis seems to be governed by one preponderant mechanism with regards to the activation energy of 1900 KJ/mol found for whatever the sintering temperature, and imply a solid-state two-dimensional nucleation growth

25 mol% of Y211 combined with small amounts of dopants leads to high performance materials, promising for levitation applications.

3. Bismuth based compound

3.1. Introduction

Taking into account one hand the fact that the quality of the precursor is of prime importance to get the desired properties for a given application and on the other hand the economically view point, different processes for powder production have been studied, in particular, in the case of Bi-2223 compositions.

In this way, a comparative study of the kinetics and phase formation of the (Bi, Pb)-2223 between solid-state, sol–gel and polymer matrix methods has been performed. The same nominal composition Bi$_{0.85}$Pb$_{0.35}$Sr$_2$Ca$_2$Cu$_3$O$_{10+5}$ has been used for the three

![Graph](image1)

Fig. 10. Critical transition temperatures for Y123 doped with Pt, Ce and Ce + Sn.

![Graph](image2)

Fig. 11. Critical current densities for Y123 doped with Pt, Ce and Ce + Sn.

![Graph](image3)

Fig. 12. Comparison between the 2223 conversion rates starting from the sol–gel, polymer matrix and the solid-state routes.
The sol–gel method precursor preparation, which leads to a dark brown powder is mainly composed of Bi$_2$CuO$_4$ and a small amount of CuO.

The mass of this powder is higher than the mass of the initial oxides, indicating that the calcination is incomplete and a direct sintering of pellets leads to Bi-2212 as a major phase. Therefore, before sintering the powder was calcined up to 730°C for 12 h to remove the remaining volatile materials. This calcined powder, principally composed of Bi$_2$CuO$_4$ and SrCaCuO, was ground by attrition, pressed into pellets (300 MPa) and sintered at 845°C for 24 h, reground by attrition and finally sintered again at 850°C for 24 h. During the second sintering, neither partial melting nor decomposition was observed. Intermediate grindings are necessary to accelerate the 2223 phase formation due to the increased reactivity of small-sized grains after attrition and to the grains rapprochement. An XRD study shows also that the effect of compaction is determinant, although the formation kinetics of 2223 does not seem to vary noticeably for a compacting stress higher than 100 MPa. After the two sintering stages, a nearly pure 2223 phase is obtained (95%) with traces of 2212. The crystallinity of the 2223 phase is rather low, but a post calcination 850°C/24 h leads to thinner XRD peaks.

The (Bi, Pb)-2223 powder was put in dense monolithic ceramics shape by sintering–forging under air. The forging cycle was optimized (temperature, load and time of maintenance) to obtain highly textured discs after a slow but significant deformation, limiting the decomposition of the 2223 phase. Nevertheless, to increase the grains cohesion the forging takes place at 845°C, temperature very close to the beginning of the 2223 phase incongruent fusion. Some secondary phases (2212, SrCaCuO, SrCaPbO), coming from an incomplete conversion of the precursor into the final 2223 powder. In order to accelerate the 2223 phase kinetics formation, an improvement of the calcination, the sintering and the intermediate grindings has been done.

The optimized heat treatment cycle is shown Fig. 14.

![Fig. 13. Reaction orders n depending on the temperature range and the synthesis process.](image1)

![Fig. 14. Schematic illustration of the heat-treatment cycle used in the sol–gel process.](image2)

### 3.2. The sol–gel method

The sol–gel method, which has shown the lowest activation energy (1000 KJ/mol), is the most promising candidate to heat treatment optimization to transform the precursor into the final 2223 powder. In order to accelerate the 2223 phase kinetics formation, an improvement of the calcination, the sintering and the intermediate grindings has been done.

The optimized heat treatment cycle is shown Fig. 14.

![Fig. 14. Schematic illustration of the heat-treatment cycle used in the sol–gel process.](image3)
3.3. The polymer matrix method

The good kinetics of formation of the Bi-2223 phase obtained with the polymer matrix method leads us to test this route for the calcination step optimization, all the more that this method has not been largely studied up to now compared to the other methods for the synthesis of the powder precursor. This route appears promising due to the large grain size, which are routinely obtained using this method [51,52]. A larger grain size allows in principal a better grain orientation during the texturation by rolling or sinter–forging. However, it has been shown that the critical current density increases when the grain size increases [53]. As the grain size and the formation of the Bi-2223, which take place during sintering, are very sensitive to the assemblage of the initial phases and to the prereactive conditions, the influence of the calcination parameters which are the temperature, time and intermediate milling has been studied.

The resulting powder prepared by the polymer matrix method [45], was crushed by hand in an agate mortar and calcined under air at different temperatures ranging from 800 to 820°C during 12–48 h. After cooling the powder was milled, pelletized (200 MPa, 16 mm diameter, 3 g), and sintered under air at a temperature of 835°C. We chose to not exceed 820°C, in order to avoid the decomposition of Ca,PbO₄ ($T_d = 822°C$) [54] which forms CaO and a liquid phase rich in Pb, because CaO reacts with CuO to form Ca,CuO [55], which in turn accelerates the nucleation of the Bi-2223 phase [56,57] and results in the formation of small Bi-2223 grains and, consequently, a weaker $J_c$ of the ceramic. The XRD patterns of the calcined powders showed that the crystallized phases mainly present at this step of synthesis are Bi-2212, Ca,PbO₄, CuO, Ca,CuO and Cu,SrO₂, which are present whatever the calcination schedule. Bi-2212 is always the major phase, accompanied by Ca,PbO₄ and CuO, but one can notice, however, that the quantities of the Ca,PbO₄ phase tend to decrease when the calcination temperature increases from 800 to 820°C. On the contrary, the Ca,CuO₃ phase increases with the calcination temperature and the Sr,CuO begins to be detected at 820°C. Bi₁₀,Ca₂,O₂₂ is present only at 800°C and for a short time. Sr₁₄,Cu₂₄,O₄₁ and Sr₁₅,Ca₀₈₅,Cu₂O₂ appear also as inter-

![Fig. 15. Optimized sinter–forging cycle and microstructure of the sinter–forged disc core.](image1)

![Fig. 16. Critical current density under magnetic field along the texture, measured in transport at 67 and 77 K, and in magnetization at 5 K (left); magnetic transitions after annealing under air or under 7.5% O₂ (right) with sol–gel precursor.](image2)
mediate phases, but disappear for a long calcination time at 820°C.

3.3.1. Influence of the calcination time at 800°C on the reactivity of the powder during sintering at 835°C

For the powder calcined 12 h, the delay in the formation of the intermediate phases at the end of the calcination is not made up for during sintering, and only 26% of Bi-2223 was formed after 60 h of sintering, and a longer calcination time at this temperature is necessary before sintering. However, the SEM observations show that the long calcination times lead to large grain size and, consequently, to a lower reactivity during sintering. For example, powder calcined for 24 h leads to a volume fraction of the Bi-2223 phase double of that calcined 48 h after 24 h sintering at 835°C. However, after a longer sintering time (60 h) one obtains the same Bi-2223 ratio for these two samples: 43% and 41%, respectively. So a longer calcination time is rather detrimental to a rapid Bi-2223 formation, and instead of increasing the time, we choose to increase the calcination temperature, with a 24 h dwell time.

3.3.2. Influence of the calcination temperature

The influence of calcination temperature (800–810–820°C) on the grain size and the formation of Bi-2223 during sintering was studied. The observation of the XRD spectra after calcination, does not reveal any large differences on the nature and the quantity of the phases present: However, the SEM photographs in Fig. 17A and B show that the grain size increases largely for a small calcination temperature increase.

During sintering, similar evolutions are observed for the powder calcined at 800 and 810°C, with about 23% of Bi-2223 after 24 h and about 45% in 60 h. On the other hand, the powder calcined at 820°C shows, in spite of a larger grain size, a much better reactivity with 50% and 79% of Bi-2223 formed in 24 and 60 h respectively. SEM photographs (Fig. 17C and D) show, once more, that a large grain size after calcination leads to a larger grain size after sintering. Finally, the results obtained after calcination at 820°C/24 h and sintering 835°C/60 h correspond to what we had anticipated, i.e. a significant grain size (>10 μm) and a large quantity of Bi-2223 (79%) form.

3.4. Conclusion

Various calcination conditions which gave rise to various phase assemblages and to various grain size, determine the rate of formation of Bi-2223 and its grain size. In order
to accelerate the Bi-2223 formation during sintering, it appears significant that the powder precursor would be calcined just below the formation temperature of Bi-2223, without exceeding its initial temperature formation. A calcined powder showing a larger grain size compared to another calcined powder, with the same phase assemblage, will maintain this larger grain size after sintering. To obtain the largest grain size at the end of the calcination (and, thus, at the end of sintering), it is also necessary to use the highest possible temperature close to 820°C. Depending on the calcination conditions, it is observed that the faster the kinetics of formation of Bi-2223 are during sintering, the larger the grain size becomes. For the polymer route the optimum time of calcination correspond to 24 h without intermediate milling. Eight hundred and twenty 5°C/24 h gave the best results during sintering with fast kinetics of Bi-2223 formation, 79% in 60 h at 835°C, and a large grain size (10 to 15 μm). The sintering and the sinter–forging of the corresponding materials are in progress.

4. Conclusions

The bidimensional structure of the HTS materials coupled with a very small coherence length dramatically restrain the superconducting performances of the classically sintered samples. One can however recover high levitation force and high $T_c$ by texturing the material in order to develop the $ab$ planes where current blow easily. MTC and derived MTC processes are very efficient in the preparation of large monoliths with different geometries. However, the precursor must be adapted to each process. In particular, the nucleation window which is closely dependent on the dopant has to be determined carefully in each case. In the case of ReBaCuO, a good central of the viscosity of the material and of the process (temperature, gradient imposed by the sample geometry, ?, very slow cooling) allows one to obtain large monodomain samples with good mechanical properties (no cracks) and a very large critical current $I_c$. In the particular case of Bi, the study of the phases formation mechanisms through the comparison of different synthesis methods allows one to accurately control the precursor purity and grain size. The sinter forging process can be now improved to developed high current capability textured ceramics. The control and the performances reached by these materials shows that they are just ready to be developed by industry.

References