Materials Research, Vol. 5, No. 2, 179-186, 2002.

Development of Bulk $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$ Superconductors by Partial-Melting Route for Fault Current Limiters Application

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Received: October 17, 2001; Revised: April 16, 2002

The production of bulk $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$ (Bi-2212) superconductors for fault current limiter application was developed via a partial-melting route. Aiming high I_c (critical current), which is the essential superconducting characteristic for application of this material in the construction of Fault Current Limiters (FCL), the produced blocks have predominance of Bi-2212 phase (83 wt%), which characterizes with high values of zero and onset transport critical temperature of 92 K and 97.5 K, respectively. A relatively low transition width, ΔT, from the superconducting to the normal state of 5.5 K, revealed a good intergrain connectivity. Consequently, current measurements on the blocks of Bi-2212 show promising I_c values of 230 A and 850 A for direct and alternate current, respectively. It is expected that further increases in the I_c values will depend on the elimination of an observed amorphous phase and further reduction of amount and grain sizes of secondary phases, still present in the blocks obtained by the proposed partial-melting route. This may be achieved by a further optimization of the partial-melting processing parameters.

Keywords: *high-temperature superconductors, Bi-2212, partial-melting, fault current limiters*

1. Introduction

After 15 years from the discovery of High-Temperature Ceramic Superconductors (HTCS)[#] there is still no application of these outstanding materials in real commercial scale, in spite of the extraordinary interest of the scientific and industrial communities in the improvement and use of these materials. At present, there is only certain sporadic utilization of the HTCS, manufactured principally by the American Superconductor Corporation (ASC) or by some other specialized manufacturer. One example of such utilization is in magnets for particle acceleration facilities, that incorporate high-temperature superconducting wires made by the ASC[1]. However, the commercial utilization of the HTCS in power transmission tapes, wires and cables, electrical motors, generators, current leads, bulk magnets in the Maglev train design and fault current limiters, which are the most desired applications of the HTCS at the present, have not yet become a reality.

This occurs due to two main reasons: the complexity of the HTCS materials and, consequently, the high cost of the present technologies for production of these materials. Nowadays, previsions for the field of superconductor industry[2] suggest that one good candidate to become the first, real commercial application of the HTCS is the fault current limiter (FCL). The present importance of a high quality FCL is based on the fact that crescent consumption of electric energy will increase the probability, in certain operational conditions, of short-circuit situations in high voltage transmission networks. Therefore, the use of the HTCS for the construction of FCL for high voltage transmission networks has been under consideration for some time. It will

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[#] The abbreviature HTCS is used due to the recent discover (Jan/2001) of superconductivity in MgB_2 with T_c of 39 K. By some authors this material could be considered as a first high-temperature intermetallic superconductor.

be an innovative device without a conventional equivalent[3]. Presently, the fault current interruption problem in high voltage transmission networks is solved with circuit breakers.

Consequently, there are various scientific groups[4-7] looking for a technology that promotes the application of the HTCS in the construction of fault current limiters. The European SUPERPOLI project[7], initiated in December 1998, is one of the most elaborated under development. It focuses on the construction of a laboratory scale device with fault current limiter properties (actually, this one has gone one step forward combining in the same device superconducting power links for high efficiency power transmission with FCL).

One of the central questions in the development of a HTCS based FCL is the choice of the proper superconducting material. There are several requirements that potential material should satisfy to candidate itself for FCL application. Principally, it must present a relatively high electric resistance in the normal state and also must be capable to carry high currents (I_c) in the superconducting state. From these basic conditions, two superconducting systems emerge as possible candidates: Bi-Sr-Ca-Cu-O (BSCCO) and Y-Ba-Cu-O (YBCO). A additional advantage of this two systems over others superconducting systems is the absence of highly toxic chemical elements in them.

At the moment, the best candidate for FCL application from the BSCCO system is the $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$ (Bi-2212) phase, because of its relatively high transition temperature ($T_c > 80$ K), phase stability and the possibility to attain high densities in the bulk form through non-conventional processing routes, for ceramics, like melting. High bulk density is an extremely important factor because it promotes high current values.

In fact, the most natural candidate for FCL application among superconducting phases from the BSCCO system would be the $Bi_2Sr_{2+x}Ca_{2-x}Cu_3O_{10+\Delta}$ phase (Bi-2223), due to its high T_c of 110K. However, its great disadvantage with respect to the Bi-2212 is the extremely limited monophasic field, resulting in a much smaller capacity of intercationic substitution and very reduced tunability of oxygen stoichiometry. Thus, the use of melting routes for production of bulk and dense forms with significant Bi-2223 content is still unsolved. Instead, there are attempts to apply some other processing routes for production of dense, bulk, Bi-2223 for FCL application. Among these, hot forging is the most promising option[8].

In the YBCO superconducting system, the phase $YBa_2Cu_3O_{7-x}$ (Y-123) is candidate for FCL application in the form of a coated film on stainless steel substrate[9]. The technique used for the film deposition is the novel and sophisticated High-Rate Pulsed-Laser-Deposition method[10]. Still, it is a expensive and complex technique for large-scale production. However, Piñol *et al*.[4] have already demonstrated a possibility to produce, by Bridgman directional solidification technique, YBCO textured bars characterized with high critical currents that could be used in construction of FCL.

In 2000, CEPEL and DCMM/PUC-Rio initiated a project, in order to develop and optimize a technology for the production of bulk $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$ (Bi-2212) superconductors for FCL application and to construct laboratory scale FCL device based on this material, operating at the temperature of 77 K.

The technology has been under development based on the partial-melting route, which had already been used in the production of Bi-2212 thick films and tapes[11-12]. The main objective of this technology is the production of bulk Bi-2212 superconductors with high superconducting transport properties, namely critical currents (I_c) and critical current densities (J_c).

There are two paths to attain high values of I_c and J_c in the Bi-2212 bulk superconductors. Firstly, there is the intrinsic way through the elevation of the critical temperature (T_c) of the Bi-2212 to a value superior, as much as possible, to the operation temperature of the FCL device, 77 K. This is the consequence of the fact that the Bi-2212 phase has a weak capacity of magnetic flux line pinning at temperatures above 30 K. Therefore, it is possible to increase the Bi-2212 pinning force capacity, at temperatures above 30K, by increasing the critical temperature (T_c) of this phase[13]. The increase of the Bi-2212 T_c's will consequently reduce depinning of the magnetic flux lines due to thermal agitation. There are theoretical[14] and experimental[15] evidences that T_c value of Bi-2212 could change over a large scale range. Namely, the $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$ manifests a possibility to have controlled and increased charge-carrier density by tuning the oxygen non-stoichiometry (Δ) and manipulating the cation composition[16]. These two mechanisms could enhance the $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$ T_c to near 100K.

The second path is the extrinsic one, aiming principally at the reduction of content and grain sizes of secondary, non-superconducting phases in the specimens and the promotion of texture, reducing the "weak-link" effect.

The partial-melting route for bulk Bi-2212 superconductors production is a rather different route in comparison to the well established melt-cast process (MCP)[17] for production of bulk forms from the Bi-2212 precursor powders. It occurs at temperatures slightly above the melting temperature of the Bi-2212 and is straightforward in the sense that does not involve casting process. Opposite to the MCP, it deals with the oxygen partial pressure sensitive peritectic melting of the Bi-2212[18], which can be illustrated as following:

$$\text{Bi-2212} \Rightarrow \text{cuprate} + \text{bismuthate} + \text{liquid} + O_2 \uparrow *$$

* The type of cuprate and bismuthate formed during the peritectic melting of Bi-2212 depends on the oxygen partial pressure.

The goal of this paper is to present some of the first results reached in the above mentioned project. It gives basics of the partial-melting route (PMR) for Bi-2212 bulk production. In addition, the results obtained so far are discussed in the light of both paths (intrinsic and extrinsic) for improvement of superconductor properties of bulk Bi-2212.

2. Experimental

2.1. Preparation of Precursor Powder

The preparation of the $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$ precursor powders with nominal compositions that favour high T_c values is the essential step. At this point, it should be stressed that poorly chosen values for x e y in the $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$ would influence negatively the superconducting properties. Majewski *et al.* discussed this principle[15,19].

Thus, the initial oxides and carbonates were mixed in appropriate proportions, homogenized and thermally treated three times at different temperatures, between 790-870 °C. The obtained precursor powders exhibit low content of secondary phases.

2.2. Partial-Melting Route

The precursor powder was mixed with a small percentage of silver powder (3 wt%) and homogenized. A bar shaped silver mould was partially filled with as-prepared precursor powder, which was then compacted. The choice of silver mould (length = 50 mm; width = 7 mm; height = 8 mm) is the consequence of the fact that silver practically does not react with the BSCCO system.

The compacted powder was submitted to the partial-melting route according to the following thermal cycle, Fig. 1.

The final product, the bulk $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$, ready to be used in the construction of FCL is presented in Fig. 2.

2.3. Characterization of the Bulk $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$

The density of the material produced by PMR was characterized by the Archimedes method. X-Ray Powder Diffraction (Siemens D-5000 with CuKα radiation, equipped with a graphite monochromator) was used for qualitative and quantitative analysis of phase composition. The internal standard method was used for Rietveld based quantitative analysis of phase content[20]. The microstructure was examined by Scanning Electron Microscopy (SEM) on Siemens-Zeiss SEM equipment with EDS attachment.

The determination of bulk $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$ superconducting properties was initiated by measurement of the critical temperature (T_c) via a.c. (magnetic) susceptibility method. Further, the critical temperature (T_c) was also determined by the electric resistance approach. The measurement of critical current (I_c) for direct current was carried out by the "four-probe" method at the temperature of 77 K. The distance of voltage contacts was of 10 mm and the nanovoltmeter used for this kind of measurements was HP-34420A. The same distance criterion was applied for measurement of the critical current for alternate current (60 Hz).

3. Results

Density evaluations of the bulk $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$ point out to high densities, around 90% of the theoretic one. This represents a gain of about 15% with respect to the conventional sintering process.

Qualitative analysis of the data obtained by X-Ray Powder Diffraction, Fig. 3, revealed that the PMR material produced following the proposed thermal cycle, Fig. 1, is not monophasic. Nevertheless, the superconducting Bi-2212 phase is the predominant one. On the other hand, there are several secondary phases in the material: the bismuthate of

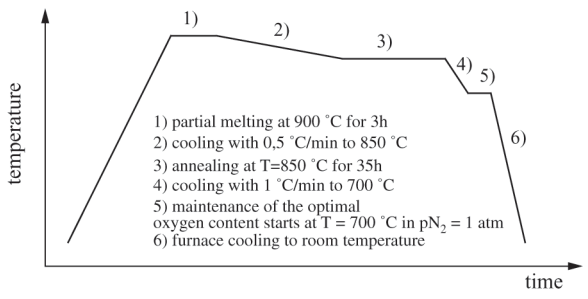

Figure 1. Applied PMR Thermal Cycle for production of bulk $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$.

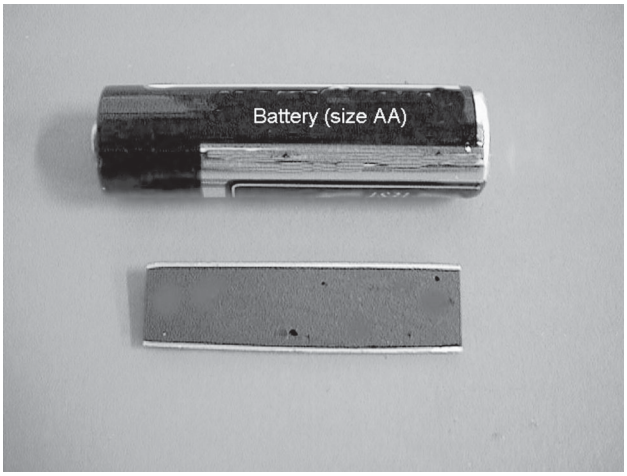

Figure 2. Block of $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$ produced by the proposed Partial-Melting Route (PMR). The battery (size AA) is included in the figure to illustrate the size of the superconducting block. The magnification of the photo is 1,5x.

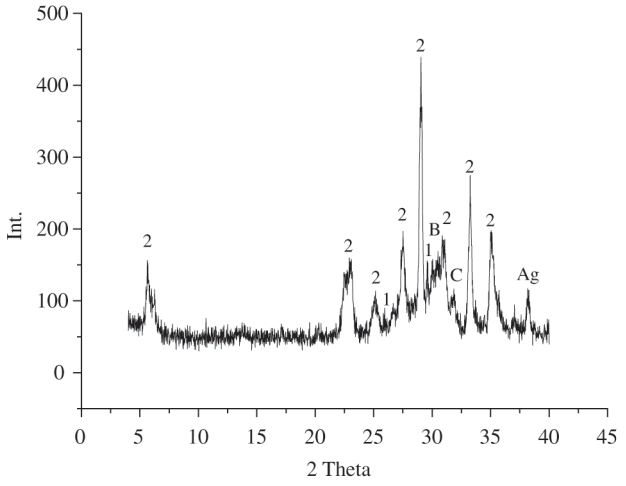

Figure 3. Diffractogram of the bulk $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$ obtained by PMR. 2: Bi-2212, 1: Bi-2201, B: 91150ss, C: 14:24-AEC, Ag: silver.

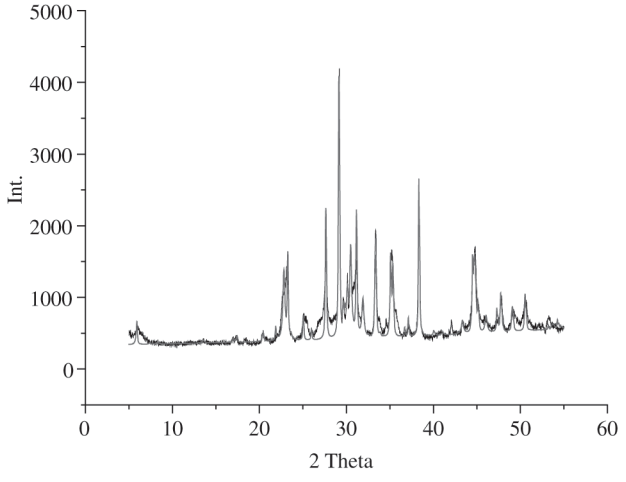

Figure 4. Difractogram of the bulk $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$ refined by the Rietveld method. The black line is the experimental diffraction profile; the red is the calculated one, based at the classical Rietveld model for background intensity contribution.

Sr and Ca, known as the 9<u>1</u>150ss phase[21,22] ($Bi_9Sr_{11-x}Ca_{9+x}O_y$ solid solution phase), the low-temperature superconducting phase $Bi_2Sr_2CuO_{6+\Delta}$ (Bi-2201), the cuprate - $(Sr,Ca)_{14}Cu_{24}O_{41}$ (known as 14:24-AEC) and silver.

A Rietveld based quantitative analysis using the internal standard method was applied. Silver powder was added at the known percentage, as the internal standard, to the pulverized material obtained through the PMR. The analysis provided two relevant informations about the phase composition of the bulk PMR obtained material, Fig. 4. The first one is that the desired Bi-2212 phase is present at a level of about 83 wt%. Secondly, there is evidence suggesting the presence of some amorphous material. Namely, applying the typical Rietveld model for refinements of purely crystalline materials[20] to this specimen, there is always some background contribution which is left over. In typical Rietveld refinements of purely crystalline materials the observed diffraction intensities (y_{obs}) could be simulated by summing crystalline Bragg scattering (y_c) and background scattering (y_b):

$$y_{obs}(Q)_= y_c(Q) + y_b(Q)$$

where $Q= 4\pi\sin\theta/\lambda$ is the magnitude of the scattering vector. In this case, the background scattering contribution is principally due to thermal diffuse scattering (TDS), as well as incoherent and air scattering. This type of background scattering is the most commonly fitted with low-order polynomial function. In our case, it was not possible to fit the background scattering contribution with some low-order function, as could be seen from Fig. 4, but only with some high-order (four or higher) polynomial function. Recently, it was shown[23] that the background contribution in diffraction patterns of the Bi-2212 produced by melting routes could be non-linear. The authors[23] always attributed non-linear background to the presence of amorphous material in the samples when the order of polynomial function used for background fitting is higher than three. From the discussion on background modelling in Rietveld method[24], the background contribution which is not accounted for by low-order polynomial function is ascribed to the "non-crystalline intensity contribution" due to presence of amorphous material. The presence of certain percentage of amorphous material in the Bi-2212 partial-melt thick films has already been observed by TEM[11] and it may be expected that the same may occur in bulk form processed by partial-melting route.

Microstructural analysis revealed some texture near the mould walls, Fig. 5. Grain orientation is a desirable microstructural characteristic for HTCS since it benefits high I_c values, reducing the "weak-link" problem[25]. In addition, the MEV/EDS technique endorsed the existence of some low content of the cuprate - $(Sr,Ca)_{14}Cu_{24}O_{41}$ (14:24-AEC) - as a secondary phase, Fig. 6.

The critical temperature of the superconducting Bi-2212 was determined, firstly, by magnetic susceptibility, Fig. 7. This measurement showed that the as-prepared Bi-2212 is superconducting exhibiting a high T_c (92.5 K). Nevertheless, the principal preoccupation in preparation of bulk superconductor is the achievement of a percolation network between superconducting grains which make possible the transport of high currents through the bulk specimen. The confirmation of the existence of this network condition is possible through measurement of T_c by electric resistance,

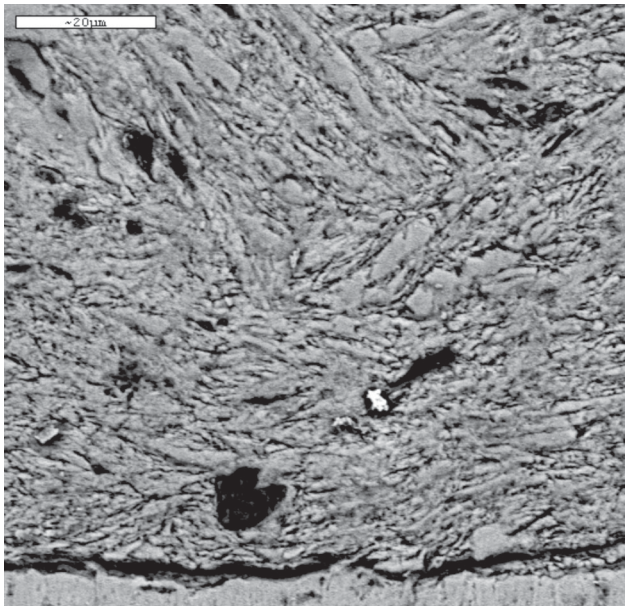

Figure 5. SEM micrograph of the microstructure of PMR bulk $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$ illustrating the presence of texture close to the mould walls.

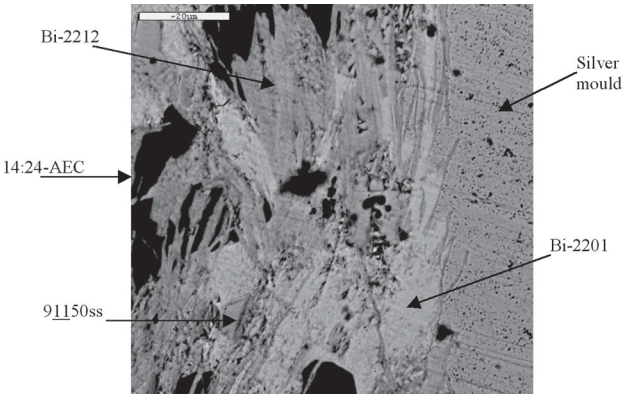

Figure 6. SEM micrograph of the microstructure of PMR obtained bulk $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$ illustrating presence of $(Sr,Ca)_{14}Cu_{24}O_{41}$ (14:24-AEC).

Fig. 8. The electric resistance measurement of our specimens revealed high values for $T_{c,zero}$ and $T_{c,onset}$ of 92 K and 97.5 K, respectively. Also, the specimens are characterized by relatively small range of superconducting transition, from normal to superconducting state, approximately $\Delta T = 5.5$ K, indicating good intergrain connectivity.

The determination of I_c for direct current was carried out by the "four-probe" method at 77 K, Fig. 9. The results, $I_c = 230$ A and $J_c = 850$ A/cm^2, exhibit promising performance of the bulk Bi-2212 for FCL application, prepared by

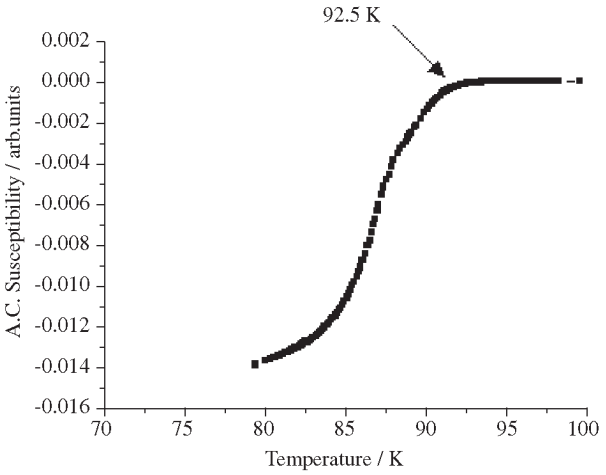

Figure 7. Temperature dependence of magnetic susceptibility for the $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$ phase obtained by PMR.

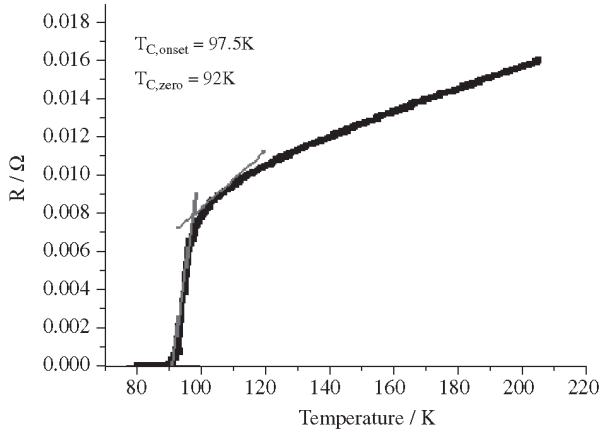

Figure 8. Resistance versus temperature for the $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$ phase obtained by PMR.

PMR. The non-zero voltage at the low currents observed at Fig. 9 is an experimental artifact due to thermal drift effect.

However, the measured I_c for alternate current at 60Hz showed much larger value, $I_c = 850$ A*, Fig. 10. Therefore, the calculated current density for alternate current is $J_c = 3150$ A/cm^2.

4. Discussion

As it was stressed earlier, the high superconducting properties in bulk Bi-2212, like high I_c, could be reached by two following paths. The intrinsic one, increasing the T_c value of Bi-2212 (and consequently, increasing the difference between the device operation temperature and the T_c of the Bi-2212, while reducing at the same time the depinning ef-

* *Root mean square* value.

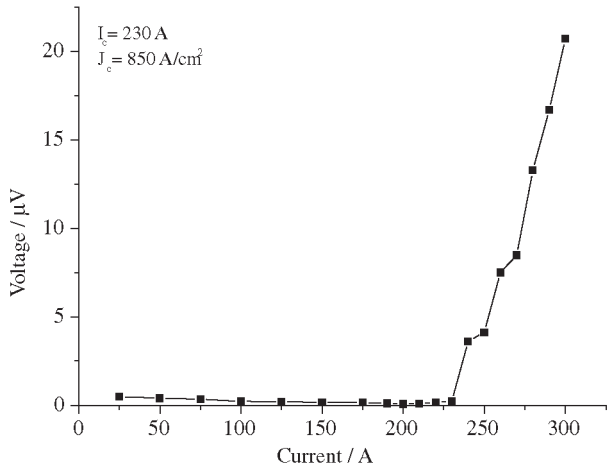

Figure 9. I_c for *direct* current in the bulk $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$ material obtained by PMR.

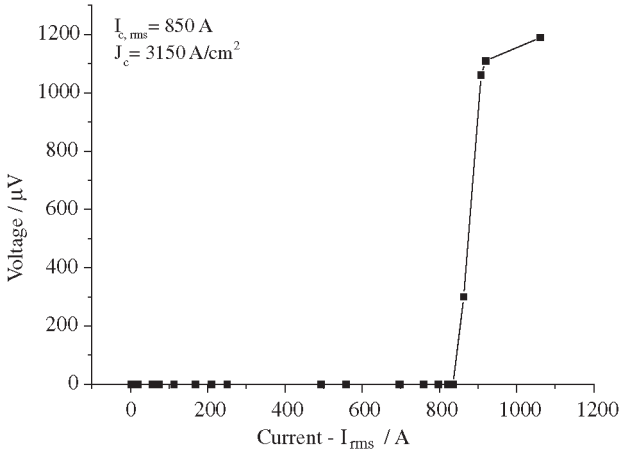

Figure 10. I_c for *alternate* current in the bulk $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$ material obtained by PMR.

fect) and the extrinsic one, which aims principally reduction of the secondary phases content and their grain sizes and possible texture formation.

So far the primary goal has been to optimize the thermal cycle of the PMR, with the intent to achieve the highest possible values of T_c for Bi-2212 phase. This phase was originally reported as possessing a T_c of 80 K[26], but some evidence has appeared recently indicating that the real genuine critical temperature value of this phase is much higher and could be close to 100 K[14,15,27]. Besides proper choice of cationic relation between Bi, Sr e Ca, it is necessary to reach an optimal value of excess oxygen, Δ, in the $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$[28], in order to achieve values of T_c above 90 K. The optimal value of excess oxygen in this phase is indicated by an onset critical temperatures of about 95 K. In this study, it is reported $T_{c,onset}$ of about 97.5 K. In order to attain such a high value, it was necessary to reach the right balance of oxygen and nitrogen partial pressures during the whole thermal cycle, Fig. 1. The high oxygen partial pressure, during part of the process, is necessary to suppress exaggerate loss of oxygen during the peritectic melting of Bi-2212, and should be reduced adequately during the cooling to preserve the Bi-2212 in the optimal hole-doped region.

The addition of small amount of silver powder also contributes to the observed values of T_c, Figs. 7 and 8. It is known that partially melt of Bi-2212 with Ag powder can dissolve more oxygen during the peritectic melting, reducing in this way the loss of oxygen from the partial-melt[29]. This oxygen has a beneficial effect on the reconstruction process of Bi-2212 during solidification of the partial melt (this reconstruction process involves reactions between the melt, solid secondary phases – bismuthates and cuprates – and the oxygen from the employed atmosphere in the process). In addition, silver powder may improve the connectivity between the superconducting grains by the so-called proximity effect[25,30] and, consequently, reduce the negative "weak-link" influence. At the same time, it may help in the alignment (texture formation) of Bi-2212 grains[25].

Therefore, it can be concluded that the achievement of high T_c values in the Bi-2212 phase during PMR depends, mainly, on: a) right cationic ratio choice, b) switch from rich to oxygen poor partial pressure (optimal oxygen tuning) and c) addition of Ag powder.

The T_c value reached during our PMR, suggests that a well-adjusted PMR could lead to near genuine values of T_c for Bi-2212, as obtained by Badeche *et al.*[27] in a single crystal of the Bi-2212.

It is appropriate to discuss now some extrinsic parameters that have also effect on I_c. The most critical extrinsic parameters influencing the critical current (I_c) of bulk Bi-2212 obtained by the PMR are the percentage of secondary phases, their grain sizes and the resultant texture.

The established thermal cycle of PMR, Fig. 1, has several important processing parameters to be optimized.

First, an attempt should be made to reduce the presence of secondary crystalline and amorphous phases, which amounts to around 17% as indicated by the results of X-Ray Powder Diffraction, Figs. 3 and 4. This factor may limit the critical current in the present bulk Bi-2212 specimens due to the partial interruption of the percolation of superconducting grains. Despite the fact that the nominal composition of the precursor powder was chosen to be in the monophasic region of the phase diagram[19], the used parameters of the thermal cycle did not permit complete

reconstruction of the Bi-2212 from the partial melt. Thus, some special attention should be paid to the optimization of processing parameters such as the temperature for partial melting and the time of permanence at this temperature. The cooling rate from this temperature to the temperature of 850 °C and the time of permanence at 850 °C (chosen due to relatively large monophasic field of Bi-2212) should also be investigated. If these four parameters are optimized, there is a chance that the percentages and mean grain sizes of secondary phases can be decreased[11,12]. A detailed study of the influences of these four parameters on the type and percentage of secondary phases in the bulk specimens, as well as on their mean grain sizes is under way.

A second concern is related to the grain alignment in the bulk specimens. Fig. 5 shows that some degree of texture is observed in the regions near the silver mould walls. However, it may be expected that further optimization of the above mentioned processing parameters could result in more pronounced texture. Still, one could consider, based on Fig. 5, that the texturization in the bulk form is connected to the sample thickness.

5. Conclusions

A technology for production of bulk $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$ superconductors for FCL application is under development, based on the partial-melting route (PMR).

The bulk Bi-2212 specimen produced by proposed PMR has high zero and onset T_c values of 92 K and 97.5 K, respectively.

The bulk $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$ superconductor obtained by PMR has promising transport properties for FCL application. The critical current values obtained for direct and alternate currents were 230A (J_c = 850 A/cm^2) and 850 A (J_c = 3150 A/cm^2), respectively.

The factors that currently limits higher I_c values are of extrinsic nature such as higher secondary phase content and relatively low texture.

Further optimization of the processing parameters, such as the temperature for partial melting and the time of permanence at this temperature, the cooling rate from this temperature to the temperature of 850 °C and the time of permanence at the 850 °C, should result in a substantial progress of the critical current of bulk $Bi_{2+x}Sr_{3-y}Ca_yCu_2O_{8+\Delta}$, aimed for construction of FCL devices.

Acknowledgements

The authors are grateful to CNPq and FAPERJ for the financial support. We thank A. Polasek for valuable discussion. The authors also express their appreciation to R. P. Silva for the technical assistance in the X-ray diffraction experiments, and to S.P. Barros, M.B. Simonson, M. B. Lisboa for the metallographic preparation of samples for SEM and the technical assistance during SEM analysis.

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