

Synthesis of Bi-based superconductor by microwave-assisted hydrothermal method

R. G. Lima¹, V. D. Rodrigues¹, C. L. Carvalho¹, S. R. Teixeira², A. E. Souza² and R. Zadorosny¹

¹Depto de Física e Química, Faculdade de Engenharia de Ilha Solteira, Univ Estadual Paulista - UNESP, Caixa Postal 31, 15385-000, Ilha Solteira, SP, Brazil

²Depto de Física, Química e Biologia, Faculdade de Ciências e Tecnologia, Univ Estadual Paulista - UNESP, Presidente Prudente, SP, Brazil

rafazad@yahoo.com.br

Abstract. In this work we studied the synthesis of BSCCO-2212 superconducting phase associating a quite similar method developed by Pechini with the microwave-assisted hydrothermal method. To study the influence of the microwaves on the properties of BSCCO system, we synthesized two samples by such method. For one sample we used carbonates and for the other one we used nitrates as chemical reagents. We also produced a reference sample just using carbonates by Pechini's method to compare their morphological and superconducting properties. The structural properties of the samples were analyzed by scanning electron microscopy and X-ray diffraction. The Bi-2212 phase is predominant in all samples and despite the nitrates-like sample has a broader distribution of grain size in comparison with the reference sample, its magnetic behaviour is closer to that presented by the reference one.

1. Introduction

Studies of new routes to synthesized oxide superconductors are focused on the production of materials with higher T_c and J_c [1,2]. Chemical methods as sol-gel, Pechini, coprecipitation and hydrothermal have been applied on the synthesis of superconducting materials due to the homogeneity to produce samples. [1,3] Thereby, on the last years, the use of microwaves in the synthesis of a variety of materials has been raised in areas as chemistry, condensed matter physics and materials engineering. In some researches, the use of domestic microwave-oven in scientific activities has been of great interest due to its simplicity and low cost operation [4]. It is interesting to emphasize that several inorganic oxides, including the CuO, absorbs micro-wave radiations as those produced by domestic microwave-oven, i.e., with frequency of 2.45GHz. Baghurst and coworkers [6] were the pioneers on the application of microwaves to synthesize mixtures of metallic oxides with superconducting properties. In such samples, the heating process begins in the inner of the copper oxides and then the heat is transferred to the vicinity. Thus, the crystallization temperature of the material is reached faster than in conventional heating processes, saving time and energy. [5,6]

Particularly, in the microwave-assisted hydrothermal method, MAH, those waves interact with the solution and part of the electromagnetic energy is converted in thermal energy. Thus, this heat is generated in the inner solution and homogeneously propagates to the entire system promoting an



extremely fast crystallization kinetics. [7,8] In contrast with the conventional heating process, there are several advantages in use MAH such as the high heating ratios which are reached, reduced processing time, energetic efficiency, formation of nano-sized grains in many cases, and so on. [8]

Thus, in this work we synthesized samples of the BSCCO system, focused on the 2212 phase. [9] We used the polymeric precursor method developed by Pechini, MP, associated to MAH. In one hand we worked with a chemical method which is a good synthesis route to produce homogeneous materials [1,3] and on the other hand we added a step on the synthesis process which consisted in the use of MAH.

2. Materials and methods

We focused on the synthesis of Bi-2212 due to its chemical stability and absence of toxic elements. We had already worked with different kind of chemical reagents, i.e., we used carbonates and nitrates. Thus, the samples were synthesized following PM and an association of PM with MAH. It was used a molar ratio of 3/1 for citric acid/metal and a mass ratio of 40/60 for citric acid/ethilenoglicol. [10].

A reference sample, REF, was synthesized by PM where we used carbonates as $(\text{BiO}_2)\text{CO}_3$, SrCO_3 , CaCO_3 and $\text{CuCO}_3(\text{OH})_2$ [11]. Another sample was also prepared using carbonates however, after the formation of the polymer, the precursor solution was submitted to MAH. The equipment used in this stage was a commercial microwave oven adapted with a Teflon[®] autoclave in which was inserted a collector cup. Such system is constituted by a thermocouple, a silicone sealing gasket, fixing screws, pressure gauge, safety valve and temperature controller. The synthesis was carried out using a heating rate of $2^\circ\text{C}/\text{min}$ and maintained at 140°C for 60 minutes. During the heating process, the registered pressure was 3 bar. After that, the solution was kept in rest for during 24 hours and all the process was repeated once more. Thus, a supernatant material and a dark brown and viscous precipitate were originated. The precipitate was isolated and dried at 70°C during five days in an oven. The resulting sample was labeled as CMAH. A third sample was produced using nitrates as $\text{Bi}_5\text{H}_9\text{N}_4\text{O}_{22}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ for which was followed the same procedure as described above to obtain CMAH. This sample was labeled NMAH.

All powders were calcinated at $200^\circ\text{C}/1\text{h}$ and $400^\circ\text{C}/2\text{h}$. After the calcinations, the powder was heat treated at 850°C [12] in two steps, one of them for 2h and the other one by 6h. The heating rate used was $2^\circ\text{C}/\text{min}$. The materials were characterized by x-ray diffraction, XRD, (Shimatzu model XRD-6000) and scanning electron microscopy, SEM, (ZEISS model EVO LS15). The XRD measurements were done in the 2θ ranged from 4° to 60° with $1^\circ/\text{min}$, steps of 0.02° and $\lambda=1.542 \text{ \AA}$ with $\text{CuK}\alpha$ radiation.

The powders were pelletized and sintered at 845°C for 24h in air. After that, the samples were characterized by XRD, SEM and electric and magnetic measurements. The four-dc probe method was used to do the electric measurements which were carried out in a home-made system consisted of a current source Keithley 228A; a multimeter Keithley 2000, a nanovoltmeter Keithley 2182 and a Dewar with liquid nitrogen. The magnetic measurements were carried out in Quantum Design PPMS model 6000.

3. Results and discussion

3.1. XRD and SEM characterizations

The XRD indicates that REF is a polyphasic sample with the presence of the Bi-2212 phase and, at least, the $(\text{BiO})_2\text{Sr}_2\text{CaCu}_2\text{O}_6$ secondary 2212 phase, as shown in Figure 1(a). For the CMAH sample, the XRD data show two phases, Bi-2212 as major phase and Bi-2201 as second phase (see Figure 1(b)). The sample NMAH has the Bi-2212 phase with traces of Bi-2201 phase and other spurious compositions such as SrCuO_2 and $\text{Bi}_2\text{Sr}_3\text{O}_6$. Those analysis were made using JCPDS cards or equivalent.

Figure 2 shows SEM images of the as obtained powders and pellets using REF, CMAH and NMAH processes. In all cases were observed plate-like grains that are characteristic of the BSCCO

superconducting system [13]. Figure 2 shows SEM micrographs of the pelletized samples. As can be observed, in this figure, the REF sample presents plate-like grains with dimensions higher than $2 \times 10 \mu\text{m}^2$ and several small rounded grains with minimum dimensions around $1 \times 2 \mu\text{m}^2$; in CMAH sample micrograph could be identified few grains with minor sizes of the order of $1 \times 1 \mu\text{m}^2$ even with thickness around 250 nm and the NMAH present plates higher than $2 \times 4 \mu\text{m}^2$ and few long needles with dimensions around $1.3 \times 16 \mu\text{m}^2$ which indicates that such sample has a broader distribution of grain size.

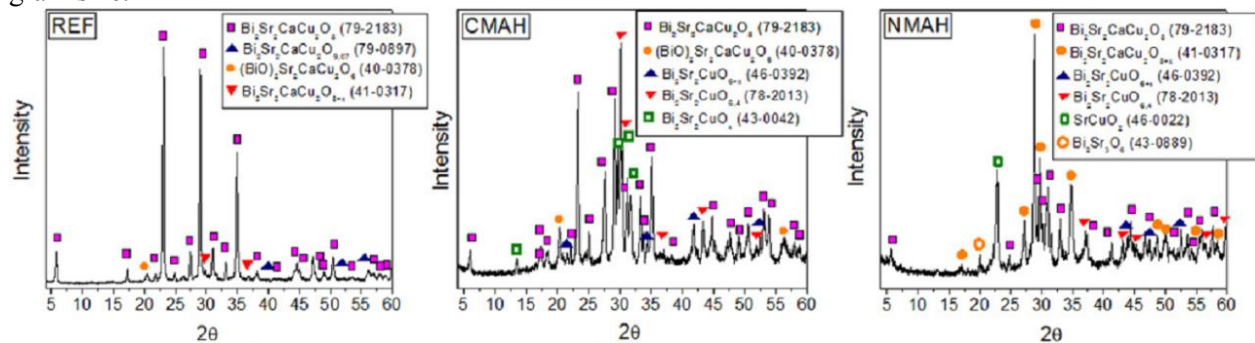


Figure 1. X-ray diffractogram of the samples REF, CMAH and NMAH.

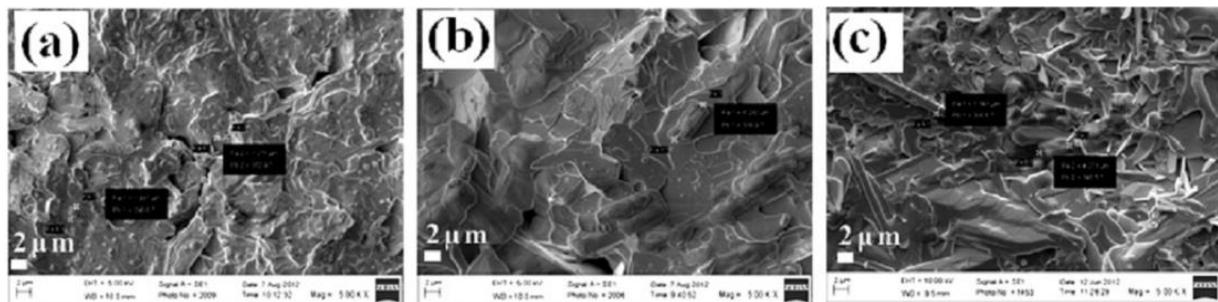


Figure 2. SEM micrographs of the pelletized samples (a) REF, (b) CMAH and (c) NMAH.

3.2. Electric and magnetic characterizations

Figure 3 shows the $R(T)$ curves of the samples. In the worked range of temperatures can note some transitions in REF at 86K, 81K and 78K. The CMAH presents a transition at 81K and the NMAH sample also presents several transitions at 92K, 90K, 85K and 80K. For all samples can note the T_c signature of the Bi-2212, as observed in the XRD analysis. The several transitions presented by all samples could be due to the presence of other superconducting phases with different T_c 's.

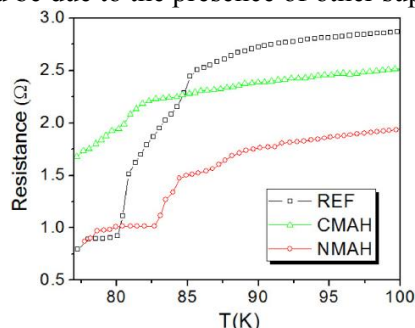


Figure 3. Resistance as a function of the temperature curves of the samples REF, CMAH and NMAH. The several transitions presented by each sample is an indicative of the presence of different superconducting phases.

Figure 4 shows the $M(T)$ curves of the samples. In all curves the T_c is around 80K, characteristic of the Bi-2212 phase. It should be noted that the zero field cooled, ZFC, curve of REF has a greater diamagnetic response, in modulus, than for CMAH. Such behaviour is an indicative that the intergranular current flows through REF easier than in the CMAH. We can also note that the NMAH sample has a response quite different from that presented by REF, probably associated to its large

grain-size distribution observed in SEM micrographs. However, the magnitude of its magnetization signal is comparable with that of the REF sample.

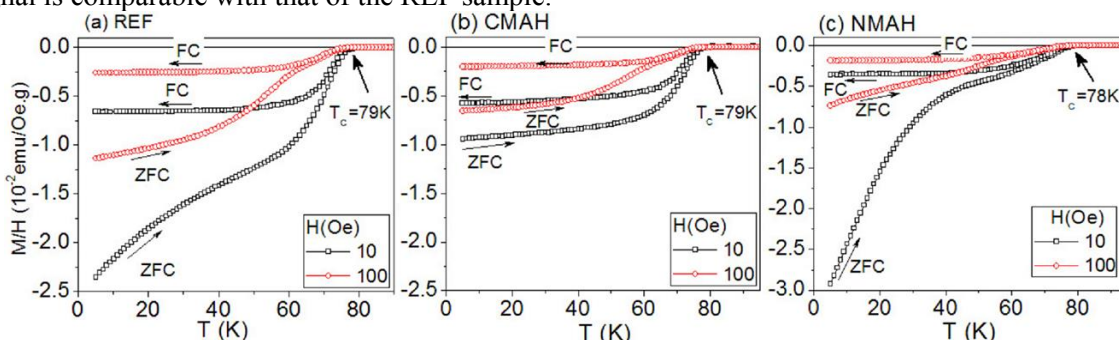


Figure 4. Magnetization versus temperature curves of the studied samples.

As conclusions we can note that both methods used in the synthesis of the samples produced the Bi-2212 phase with segregate phases. SEM micrographs show the presence of at least two type of grains, i.e., a plate-like grains which are characteristic of BSCCO superconducting system and rounded grains. In the electric characterizations, the several transitions presented by some samples could be related to other superconducting phases. The differences between electric and magnetic responses might be related to the fact that while the surface response is predominant in electric characterizations the magnetic ones measure an average response of the bulk sample. The measurements of the magnetization versus temperature followed the ZFC and FC procedures of the REF and NMAH samples corroborates with the SEM observations, i.e., the broader distribution of grain size could be responsible to the different behaviours exhibited under external magnetic fields. Thus, it can be concluded with those analyses that the sample produced only by Pechini's method present a better superconducting response than the samples produced by MAH. However, between MAH samples, the sample produced by nitrates, NMAH, presented a behaviour closer to that presented by REF sample. It is worth to emphasize that this is an initial study of the production of oxide superconductors by the microwave-assisted hydrothermal method.

We thank the Brazilian Agencies CAPES, CNPq, Fundunesp/PROPE and the São Paulo Research Foundation (FAPESP), grant 2013/11114-7, for financial support.

References

- [1] Rao, C N R, Nagarajan R. and Vijayaraghaven R 1994 *Superc. Sci. Techn.* **6** 1
- [2] Deimling C V, Motta M, Lisboa-Filho P N, Ortiz W A 2008, *J. Mag. Mag. Mat.* **320** e507
- [3] Zhang Y, Yang H, Li M, Sun B and Qi Y 2010 *Cryst. Eng. Comm.* **12** 3046
- [4] Keyson D, Longo E, Vasconcelos J S, Varela J A, Éber S, Dermaderosian A 2006 *Cerâmica* **52** 321
- [5] Volanti D P, Cavalcante L S, Keyson D, Lima R C, Moura A P, Moreira M L, Macario L R, Godinho M, 2007 *Metalurgia & Materiais* **63** 351
- [6] Baghurst D R, Chippindale A M and Mingos D M P 1988 *Nature* **332** 311
- [7] Souza A E, Silva R A, Santos G T A, Moreira M L, Volanti D P, Teixeira S R, Longo E 2010 *Chemical Physics Letters* **488** 54
- [8] Zhu X H and Hang Q M 2013 *Micron* **44** 21
- [9] Maeda H, Tanaka Y, Fukutumi M and Asano T 1988 *J. Appl. Phys* **27** L209
- [10] Chu C T and Dunn B 1987 *J. Am. Ceram. Soc.* **70** C-375
- [11] Kakihana M 1996 *Sol-Gel Sci. Tech.* **6** 7
- [12] Peng Z S, Hua Z Q, Li Y N, Di J, Ma J, Chu Y M, Zhen W N, Yang Y L, Wang H J and Zhao Z X 1998 *Journal of Superconductivity* **11** 6
- [13] Majewski P 2000 *Journal of Materials Research* **15** 4