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Synthesis of (Bi,Pb)-2223 superconductor powder by Pechini method

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ABSTRACT

In this paper, we present a detailed route of synthesis to produce ceramic superconductor $Bi_{1,6}Pb_{0,4}Sr_2Ca_2Cu_3O_x$ (Bi,Pb)-2223 powder by Pechini method. The obtained polymeric precursor solution was produced by using inexpensive chemical reagents, which showed a great stability for three weeks with high concentration of BPSCCO inorganic ions. The crystallization kinetic of BPSCCO powder was investigated by thermal analysis (DSC/TGA) and X-ray diffraction (XRD) techniques. The thermal treatment of the BPSCCO powder at different temperatures showed that complex phase equilibrium occurs to the system. The three superconductor phases seems to coexist in a large range of temperature, the Bi-2201 phase was crystallized around 500 ^{o}C and then, after 840 ^{o}C the desirable (Bi,Pb)-2223 phase appears with coexistence of the Bi-2212 phase at low quantity. Finally, the powder morphology was characterized by scanning electron microscopy (SEM), the results point to a typical plate like formation of the grains.

PALAVRAS-CHAVE: Bi-2223 superconductor; Pechini Method; Low cost synthesis.

INTRODUCTION

Extensive studies have been made in new routes to synthesized oxide superconductors, mainly focused on improve the superconductor properties, such as higher critical temperature (T_c) and great electrical current density (J_c) (OHARA *et al*., 2015; SAFRAN *et al*., 2015; FREITAS *et al*., 2016-a). The BSCCO system - $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n+y}$ (n = 1, 2, 3 or 4), is one of the main high temperature superconductors, and have been extensively investigated for technological applications and basic studies in materials science since its discovery by Maeda *et al*. (1988). The BSCCO system presents three different crystallographic phases with superconductor properties. In general, the $Bi_2Sr_2Ca_1Cu_2O_x$ (Bi-2212) is the most studied composition, because it´s present great superconductor properties and a relatively facile synthesis compared with other systems. The Bi-2212 have been produced by a large variety of techniques and different morphologies, such as films, bulk, wires, tapes and fibers (FREITAS *et al*., 2015; CENA *et al*., 2017 FREITAS *et al*., 2016-b). Although, the $Bi_2Sr_2Ca_2Cu_3O_x$ (Bi-2223) superconductor phase is well known as a difficult stoichiometry to obtain, mainly due to an unstable phase equilibria, what makes it less explored for many research groups, who are dedicated to produce superconductor materials for basic studies and applications (PANDEY *et al*., 1990). However, the Bi-2223 is one of the most suitable for technological applications due to its higher critical current density (Jc) and critical temperature (Tc), when compared with the Bi-2212.

Regarding the superconductor phases of the BSCCO system, the Bi-2201 is the more common and stable phase, with Tc around -253 ^oC, presenting low crystallization temperature between 400 ^oC and 650 ^oC. The Bi-2212, considered a stable phase, exhibits Tc usually around -188 ^oC and its crystallization occur between 730 ^oC and 840 ^oC (WONG *et al*., 1992; MAJEWSKI, 1997). Finally, the Bi-2223 phase, with Tc around -165 ^oC, it is considered an unstable phase, because presents a short crystallization temperature range between 840 ^oC and 850 ^oC. Moreover, there is a complex multiphase equilibrium involved during the phase formation, that usually drives the system to secondary phases formation, such as $(Ca,Sr)_2CuO_3$, CuO and Ca_2PbO_4, and disturbs the aligning and coupling of superconductor plates (WANG *et al*., 1998; JIANG *et al*., 2001). Some studies, devoted to produce pure Bi-2223 phase have shown that the kinetic and stability of the phase formation can be improved by doping the system with lead ions (Pb+). The Pb ions replace Bi ions in the C-site, extending the crystallographic structure, and facilitating, the growth of new plane of Cu and Ca (TAKANO *et al.*, 1988; TAKEDA *et al.*, 1989).

Extensive studies have been made in new routes to synthesized oxide superconductors in the past few decades, mainly focused on improve the superconductor properties, such as higher critical temperature (Tc) and great electrical current density (Jc) (OHARA *et al.*, 2015; SAFRAN *et al.*, 2015; FREITAS *et al.*, 2015). In this context, there is many advantages of produce (Bi,Pb)-2223 by Pechini method (LESSING, 1989), such as, (i) the method is able to produce thinner powder from a homogeneous reagent mixture, thereby increasing the reactivity of the powder; (ii) the low cost and simple laboratory facilities are required; (iii) great potential to produce many types of samples, such as thin films, nanoparticles, nanofibers, from a polymeric resin; and finally (iv) there is a facility to introduce others ions in the structure or even produce composite materials for basic studies and/or applications.

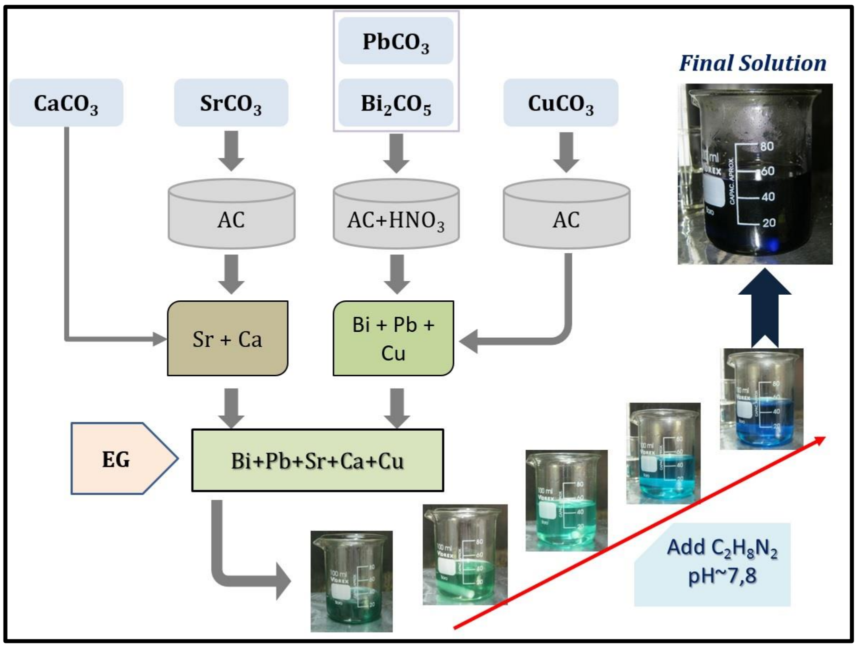
In this work, we present a detailed route for processing (Bi,Pb)-2223 powder by Pechini method. The dynamic viscosity studies of the resulting polymeric resin were performed to investigate the solution stability. The BPSCCO dried powder was studied by thermal analysis (TA), and after thermal treated at different temperatures, the phase evolution, microstructure and crystallographic phase formation of the samples were studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively.

EXPERIMENTAL DETAILS

The BPSCCO powder with nominal composition $Bi_{1,6}Pb_{0,4}Sr_2Ca_2Cu_3O_x$ was obtained by Pechini method (LIMA *et al*, 2014). As starting materials was employed carbonates (Bi_2CO_5, $SrCO_3$, $CuCO_3$, $CaCO_3$, $PbCO_3$) all purchased from VETEC Chemical Company Ltd. A stable resin was obtained by dissolving, separately, the starting materials in deionized water and citric acid ($C_8H_8O_7$) (AC) at room temperature. The metallic ion/citric acid ratio employed was 1/3.

The ion solutions mixtures followed the steps described in the **Figure 1**. Then, ethylene glycol ($C_2H_6O_7$) (EG) was added to the solution (citric acid/ethylene glycol = 60:40 mol%) and polymerized by heating up to 80 ^oC during 30 minutes. The final pH was ajusted, by adding few drops of ethylenediamine ($C_2H_8N_2$), between 7,0 and 8,0. The pH adjust was necessary to improve the resin stability, as result the resin coloration changes from light green to a dark blue.

Figura 1- Schematic experimental route to produce (Bi,Pb)-2223 polymeric resin by Pechini method



Source: The Author.

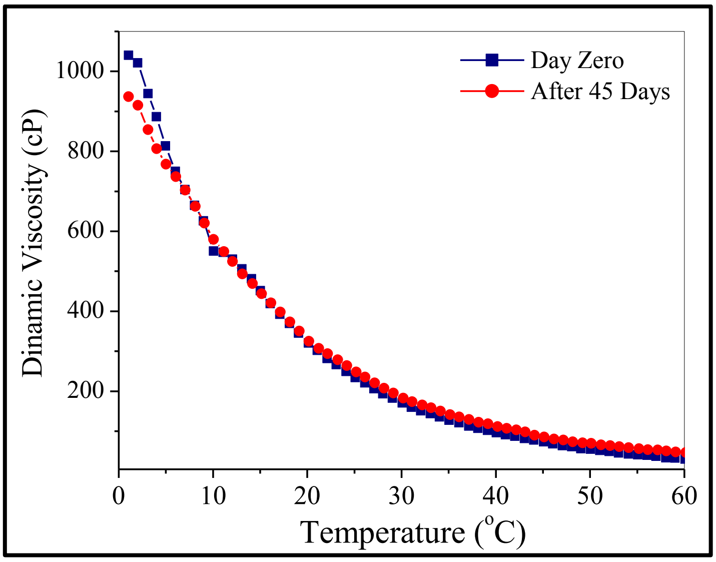
Finally, the resin was dried at 220 °C/ 1 h, and then termal treated at 500 °C/ 1 h by using a conventional electric furnace. The dried powder was grounded in an agate mortar and then, it was submitted to additional thermal treatment at different temperatures (220 °C, 500 °C, 632 °C, 705 °C, 743 °C and 850 °C), as described bellow.

The rheological properties were evaluated in a Brokfield rotameter, model DV-II+Pro, with concentric cylindrical symmetry, by measuring the dynamic viscosity in different temperatures. The thermal decomposition behavior of the as-burnt powder was examined by simultaneous Differential Thermal Analysis/Thermogravimetry (DTA/TG) in nitrogen atmosphere with heating rate of 10 °C/ min on the TA SDT instrument, model Q600. The phase identification of the calcined powders was performed using X-ray diffraction (XRD), in a Shimadzu diffractometer, model XRD-6000, with CuKα 1.54056 Å. Finally, the thermal treated samples morphology and chemical composition were evaluated by Scanning Electron Microscopy with dispersive energy detector (SEM-EDS) on the Carl Zeiss EVO-LS15 microscopy.

RESULTS AND DISCUSSION

The dynamic viscosity studies performed as function of temperature, **Figure 2**, showed a typical exponential decay of Newtonian fluids. The same behavior was observed to the resin after 45 days, suggesting a great stability. A stable resin is very important to potential applications, it guarantees the reproducibility of the samples during long period of time. The viscosity of the resin at room temperature was around 200 cP, and density of 1.28 g/ml.

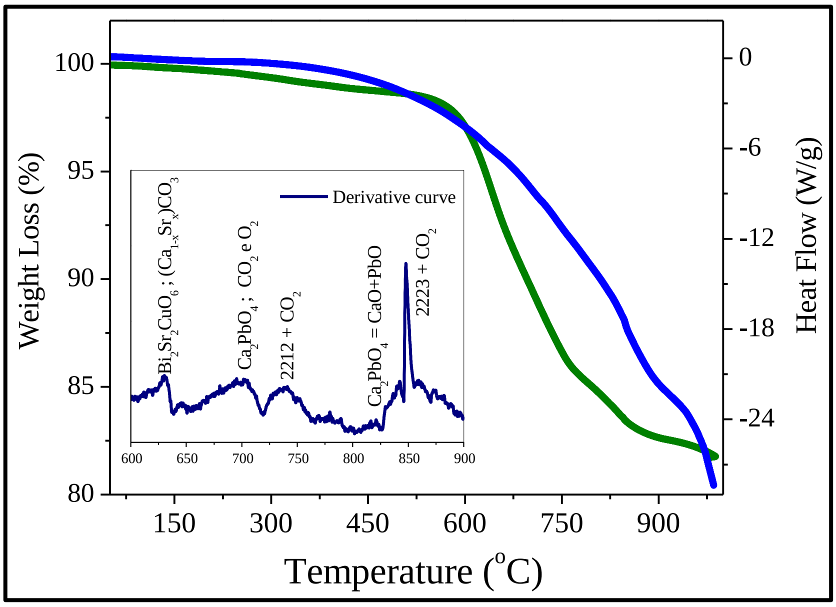
Figura 2- Rheological characterization of the BPSCCO polymeric resin produced by Pechini method. Dynamic viscosity behaviour as prepared and after 45 days



Source: The Author.

The thermal analysis measurements of the BPSCCO powder, previously treated at 500 °C/ 1 h, are showed in **Figure 3**. The TG data analysis revealed a small weight loss around 1,25 % between 200 °C and 450 °C, probably due to remaining organic material weakly bounded from polymeric chains. A second weight loss of around 17 % associated with carbonate thermal degradation was observed in two stages, a more pronounced one after 600 ^oC, a second small shoulder observed after 750 ^oC. The derivative curve, calculated from DSC curve, is also showed inset. From the DSC data and also based on XRD analysis, Figure 4, the first peak observed between 600 – 700 °C was assigned as $Bi_2Sr_{2-x}CuO_6$ (Bi-2201), $CaCO_3$ and $SrCO_3$ phases formation. By increasing the temperature of thermal treatment, the Ca_2PbO_4 phase formation was observed between 700 – 730 °C. Then, the Bi-2212 phase was formed from reaction between the Bi-2201, $CaCO_3$, $SrCO_3$ phases and Cu ions, corresponding to the third peak observed around 740 °C. Finally, around 820 °C the Ca_2PbO_4 seem to decompose in CaO and PbO, after that, upon 840 ^oC there is a tendency to crystallize the (Bi,Pb)-2223 from Bi-2212, $CaCO_3$ and CuO reaction. It is in agreement to reported by Rao *et al.* (1996).

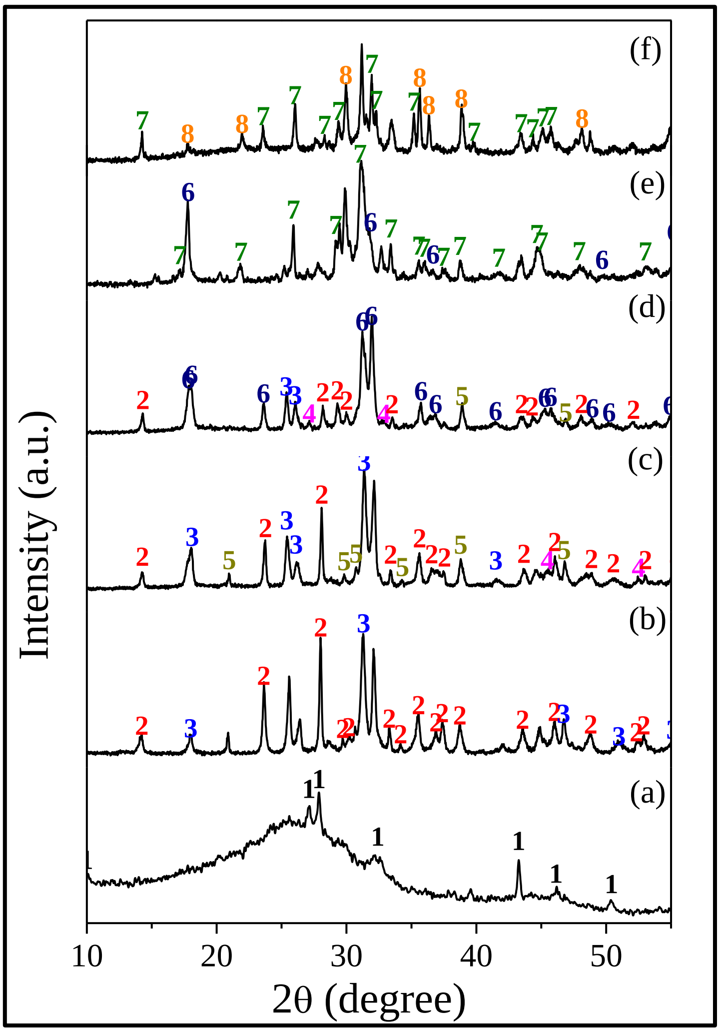
Figura 3- TGA/DSC results of BPSCCO powder, previously thermal treated at 500 ^oC/ 1 h. The derivative DSC curve inset



Source: The Author.

X-ray diffraction (XRD) patterns of the BPSCCO powder after thermal treatment at different temperatures are shown in **Figure 4**. The phase identification in the XRD patterns was performed by using crystallographic data reference from the ICSD (Inorganic Crystallographic Structure Database). At **Figure 4(a)**, a wide amorphous band, between 20^o and 35^o, related with short range ordering associated with a non-crystallized material could be evidenced, the presence of small diffractions peaks were assigned to Bi_2CaO_4 phase formation. The superconductor phase Bi-2201 formation could be identified by increasing the temperature of thermal treatment, between 500 ^oC and 632 ^oC, **Figure 4(b)** and **Figure 4(c)** respectively (TORARDI *et al.*, 1988). Although, some peaks associated with secondary phases such as $SrCO_3$ e $CaCO_3$ were also identified. These secondary phases correspond to an unreacted precursor material, that should react at higher temperatures with other elements to form another Bi-superconductor phase, the same behavior was also observed by Peng *et al.* (1998). By increasing the temperature of thermal treatment to 705 ^oC, **Figure 4(d)**, the sample showed a remarkable presence of Ca_2PbO_4 phase, this phase is considered as a secondary phase, but at 743 ^{o}C, **Figure 4(e)**, it recombines with other phases to form the Bi-2212 phase (SUNSHINE *et al.*, 1988). Finally, the XRD results observed to the powder treated at 849 ^{o}C, **Figure 4(f)**, showed the crystallization of the desirable phase (Bi,Pb) -2223, but with coexistence of Bi-2212 (YAKHMI *et al.*, 1993).

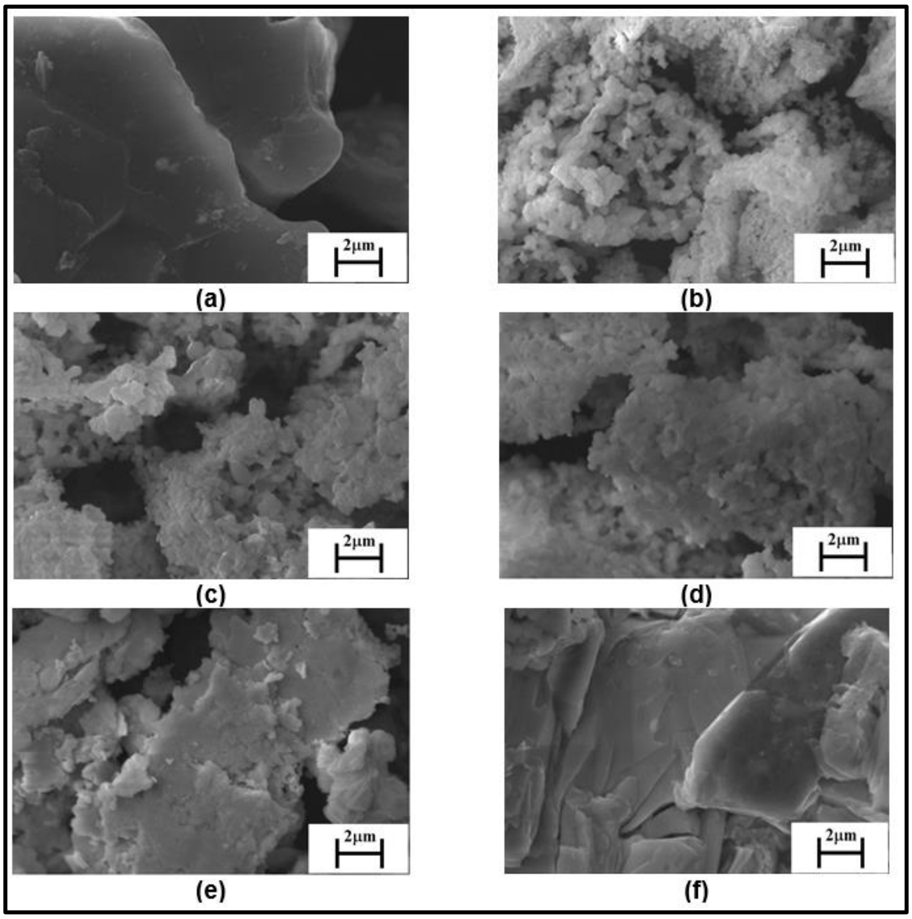
Figura 4- XRD powder diffraction at different temperatures of thermal treatment: (a) 220 ^{o}C, (b) 500 ^{o}C, (c) 632 ^{o}C, (d) 705 ^{o}C, (e) 743 ^{o}C and (f) 850 ^{o}C, during 1 hour. The peaks were indexed as: 1) $CaBi_2O_4$; 2) Bi-2201; 3) $SrCO_3$; 4) $CaCO_3$; 5) Bi_2CuO_4; 6) Ca_2PbO_4; 7) Bi-2212; 8) (Bi,Pb)-2223 phases



Source: The Author.

Images obtained by scanning electron microscopy (SEM) of the treated powders are shown in **Figure 5**. The changes on powder morphology could be successfully evidenced. As evidenced by DRX analysis, the presence of the organic material at the sample treated at 220 ^{o}C were characterized by a smooth surface, **Figure 5(a)**. By increasing the temperature of thermal treatment the organic compounds degraded, remaining just the inorganic content, which ones react to from the crystalline phases. Then, the initial smooth surface observed at 220 ^{o}C, evolves to small grain morphology typical of ceramic materials at intermediary temperature range. Finally, the morphology presents a plate-like grains structure above 743 ^{o}C, characteristic of Bi-superconductor phase, exhibiting a grain size distribution around 800 nm at 850 ^{o}C.

Figura 5- SEM images of treated powder during 1 hour at different temperatures (a) 220 ^{o}C, (b) 500 ^{o}C, (c) 632 ^{o}C, (d) 705 ^{o}C, (e) 743 ^{o}C and (f) 850 ^{o}C.



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Finally, quantitative/qualitative results from Energy Dispersive X-ray Spectrometry - EDS, are presented at **Table 1**.

Tabela 1- Atomic percentage of elements in the samples determined by EDS analysis

Temperature	220 ^{o}C	500 ^{o}C	632 ^{o}C	705 ^{o}C	743 ^{o}C	849 ^{o}C
Element	Atom %	Atom %	Atom %	Atom %	Atom %	Atom %
Bi (M)	0,56	3,40	7,78	5,63	6,36	6,94
Sr (L)	0,51	7,52	11,22	10,07	11,04	8,32
Ca (K)	0,55	8,84	11,18	9,74	10,94	14,28
Cu (K)	0,25	10,93	5,33	9,00	12,41	20,75
O (K)	15,21	48,09	64,41	65,56	59,52	49,70
C (K)	53,59	21,22	0,00	0,00	0,00	0,00
N (K)	29,33	0,00	0,00	0,00	0,00	0,00

Source: The Author.

As discussed above at low temperature treatment (~220 ^{o}C) the presence of organic compounds could be confirmed by the large presence of nitrogen and carbon in the powder. By increasing the temperature of thermal treatment, the organic material has been removed, as observed on TGA analysis, remaining just a small amount of carbon atoms at 500 ^{o}C. Above 500 ^{o}C remains just the inorganic compounds that react to form the crystalline phases. The amounts of Bi and Sr in the stoichiometry did not changed substantially by increasing the temperature, however, the amounts of Ca and Cu present considerable variation, as expected because there is an evolution of the superconductor phase (from Bi-2201 to (Bi,Pb)-2223). The Pb ions could not be evidenced at EDS analysis probably by its low content in the material, and also experimental difficulties to measure samples with irregular surfaces with quantitative precision.

CONCLUSIONS

The Pechini method presented a great potential to produce thinner BPSCCO powders, with grain size around 800 nm, from polymeric solution. The crystallization kinetics study, based on TG/DSC and XRD results, are in accordance with the literature reports to the system produced by sol-gel method. The thermal treatment of the powder indicated formation of three superconducting phases Bi-2201, Bi-2212 and (Bi,Pb)-2223. The results showed that by add Pb ions in the BSCCO precursor can induce the (Bi,Pb)-222 phase formation, providing an easy and low cost route to produce superconductor materials for academic studies.

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Síntese do supercondutor BSCCO (2223) pelo método de Pechini

RESUMO

Neste trabalho, apresentamos uma rota detalhada para preparação de pós-cerâmicos supercondutores do sistema $Bi_{1,6}Pb_{0,4}Sr_2Ca_2Cu_3O_x$ (Bi-2223) utilizando o método de Pechini. A cinética de cristalização do pó BSCCO foi estudada pelas técnicas de análise térmica e difração de raios-x. Os resultados observados revelaram a ocorrência de uma complexa cinética de formação fase no sistema, marcado pela coexistência das três fases supercondutoras do sistema BSCCO em um grande intervalo de temperaturas do tratamento térmico. A formação de fases cristalinas teve seu início em torno de 500 ^oC com a formação da fase Bi-2201, e com o acréscimo da temperatura ocorreu a formação da fase Bi-2212, a qual irá coexitir com a fase desejada Bi-2223, formada após 840 ^oC. Finalmente, a caracterização morfologica das amostras foi realizada em um Microscopio Eletrônico de Varredura, os resultados mostraram a formação de uma estrutura de grãos cerâmicos do tipo placa típica do BSCCO.

KEYWORDS: Supercondutor Bi-2223; Síntese química; Método de Pechini.

Síntesis del superconductor BSCCO(2223) por el método de Pechini

RESUMEN

En este trabajo, presentamos una ruta detallada para la preparación de polvos cerámicos superconductores del sistema Bi1,6Pb0,4Sr2Ca2Cu3Ox (Bi-2223) utilizando el método de Pechini. La cinética de cristalización del polvo BSCCO fue estudiada por las técnicas de análisis térmico y difracción de rayos-x. Los resultados observados revelaron la ocurrencia de una compleja cinética de formación fase en el sistema, marcado por la coexistencia de las tres fases superconductoras del sistema BSCCO en un gran intervalo de temperaturas del tratamiento térmico. La formación de fases cristalinas tuvo su inicio alrededor de 500 oC con la formación de la fase Bi-2201, y con el aumento de la temperatura ocurrió la formación de la fase Bi-2212, la cual coexistir con la fase deseada Bi-2223, formada después de 840 oC. Finalmente, la caracterización morfológica de las muestras fue realizada en un Microscopio Electrónico de Barrido, los resultados mostraron la formación de una estructura de granos cerámicos del tipo placa típica del BSCCO.

PALABRAS CLAVE: Superconductor Bi-2223; Síntesis química; Método de Pechini.

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