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BPSCCO Superconducting Films Grown by Spray Pyrolysis Technique: Systematic Study of the Relationship between Pb Content and Annealing Conditions

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ABSTRACT

Actually recent investigation in developing semiconducting-superconducting composites based in CdS and Bi-based superconductors has attracted interest in processing thin superconducting films. In this work are reported Bi-Pb-Sr-Ca-Cu-O (BPSCCO) thin films grown on MgO substrates by spray pyrolysis technique from a solution containing $Bi(NO_3)_3$, $Pb(NO_3)_2$, $Sr(NO_3)_2$, $Ca(NO_3)_2$ and $Cu(NO_3)_2$, with a subsequent solid state reaction for growing the Bi-based superconducting phases. Annealed films were characterized by X-ray diffraction, atomic absorption spectroscopy and resistance measurements. Interdependence between Pb content, annealing time and temperature, in the formation of superconducting phases was studied applying a fractional factorial design 3_{III}^{4-2}. Interrelation between Pb content, t_a and T_a exists. The presence of Pb is necessary to stabilize the high-T_c phase but its content depends on the annealing conditions.

Keywords: Superconductivity; BPSCCO Superconducting Films; Spray Pyrolysis Deposition; Pb Content; Annealing Conditions; Experimental Design

1. Introduction

The discovery of high-T_c superconductors has attracted much attention for their technological applications as bulk material as well as thin films, as for example, electronic devices, conductor tapes, and superconducting quantum interference devices. For the preparation of thin films, several physical and chemical techniques have been used: pulsed laser deposition [1], r. f. sputtering [2], magnetron sputtering [3], atomic layer epitaxy [4], chemical vapor deposition [5] and chemical deposition (spray pyrolysis) [6]. Most of them are high vacuum deposition techniques that produce superconductor thin films by sequential layer-by-layer deposition of the constituent elements. The precursor films obtained by means of this sequential deposition needs oxidation of the deposited layer with complete evaporation of the volatile gases present. The spray pyrolysis technique does not need subsequent oxidation because the complete thermal decomposition and oxidation of the deposited layers can be controlled [7]. On the other hand, Bi-based films are already used in low current as well as power applications [8,9]. Among the high-T_c ceramic superconductors, the Bi-based system has been extensively studied because of its high critical temperature, especially with the partial substitution of Pb in Bi and Sr sites since it promotes the stabilization of the 2223 phase when grown from the 2212 phase [10]. It has been found that the nominal composition and thermal treatment parameters such as heating rate, annealing temperature, annealing time, as well as, oxygen content play an important role in the formation of high-T_c phases and the thermodynamic stability of these phases [6]. However, it has not been reported the interdependence between Pb content, annealing temperature and annealing time on growing the high-T_c superconducting Bi-phases. The influence of the Bi content upon the critical temperature T_c values, the c-axis lattice parameter and the surface morphology of the synthesized films is also recognized. Studies of Pb-substituted $Bi_2Sr_2Ca_2Cu_3O_{8+}$ single crystals indicate a reduction in T_c values of the overdoped samples. When growing the Bi-based films, many technological parameters are involved in such a process that influences the final properties of the synthesized films. In our previous studies we observed a loss of Pb during the annealing treatment [11]. This Pb-loss led to the transformation of the high-T_c (2212 and 2223) phases to the low-T_c (2201) phase or others no superconductor phases. This phenomenon was caused by exposition of the precursor annealing in a free air ambient into which Pb evaporates. In studies done on material in volume has been reported that in the Bi-based system the partial substitution of Pb in Bi sites promotes the stabilization of the high-T_c 2223 phase for following reasons: a) Pb diminishes the melting point of the compound which is convenient for the formation of the high-T_c (2223) phase; b) Pb can have a catalytic effect and/or of stabilization for the high-T_c phase since accelerates the reaction between the phase of low-T_c and the atoms of Ca through Ca_2PbO_4 and, c) Bi and Pb tend to form Bi-O, Pb-O layers in the crystalline structure of the superconducting phases because their atomic radios are very closed. By these reasons it is important to keep the Pb in the structure in order to obtain high-T_c (2223) phase [10].

In the present work, we report on the deposition of Bi-Pb-Sr-Ca-Cu-O films using the spray pyrolysis technique and the interdependence between Pb content, annealing temperature,

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annealing time and covering material, applying a fractional factorial design 3_{III}^{5-3}.

2. Experimental Procedure

Bi-Pb-Sr-Ca-Cu-O (BPSCCO) thin films grown on MgO substrates were prepared by the spray pyrolysis technique following the two-step procedure described in detail elsewhere [6]. An aerosol atomized ultrasonically from an aqueous nitrate solution of Bi, Pb, Sr, Ca, and Cu components with a cation ratio 1.4:x:2:2:3 (where x is the nominal lead content) was sprayed for 5 min over single-crystalline MgO substrate. Three such cycles were applied with a total film thickness of approximately 5 μm. These BPSCCO precursor films were then annealed at 840ºC, 850ºC and 860ºC in air to become superconducting. The growth parameters studied by applying a fractional factorial design 3_{III}^{5-3} were covering material, annealing time (t_a), annealing temperature (T_a) and the nominal Pb content (x) before annealing. Influence of each parameter was investigated in a chosen interval for its three values i.e. minimum, medium and maximum value. Table 1 shows values of those parameters used for each experimental run. The superconducting pellets, precursor films and plate-shaped crystalline MgO were used to cover the precursor films in order to avoid the lead evaporation and to observe which type of cover helps to maintain the composition of the superconducting film most close to the nominal composition. Annealed precursor films were in direct contact with the covering material. The superconducting pellet composition was closed to $Bi_2Pb_{0.3}Sr_2Ca_2Cu_3O$; the covering precursor film composition and the composition of the investigated precursor film were the same, i.e. with the cation ratio 1.4:x:2:2:3 where x is the lead content before annealing. The chemical composition of the films was measured by atomic absorption spectroscopy. Samples were then characterized by X-ray diffraction (XRD) with CuK radiation using the Siemens D500 diffractometer. The R vs. T dependence was measured by using the standard four-point resistance method. The chemical composition was determined by measurements of atomic absorption spectroscopy using an Analyst 300 Perkin Elmer Spectrometer.

3. Results and Disscusion

3.1. X-Ray Diffraction Patterns

Figures 1 and **2** show respectively X-ray diffraction patterns from films 2 and 7. These films were prepared according to the conditions shown in **Table 1**. From **Figure 1** we observe that in order to grow the $(Bi\text{-}Pb)_2Sr_2Ca_2Cu_3O$ phase denominated Bi-Pb-2223 so as the Bi-2212 phase, an annealing temperature of 850ºC during 15 h and Pb content of 1.4 mole are required (film 2). This indicates that to obtain the high-T_c Bi-based superconductor phases, annealing temperatures smaller than 860ºC, annealing times longer than 1 h and Pb content between 0.7 and 2.1 moles are required. In contrast, for the film 7, in order to grow those superconducting phases an annealing temperature of 860ºC during 1 h and Pb content of 1.4 mole are required. At the same way, this indicates that in order to obtain the high-T_c Bi-based superconducting phases, annealing temperatures longer than 850ºC, annealing times smaller than 15 h and Pb content between 0.7 and 2.1 mole are required. Therefore it can be observed that an adequate Pb-content of 1.4 for annealing temperatures between 840ºC and 860ºC, and annealing times

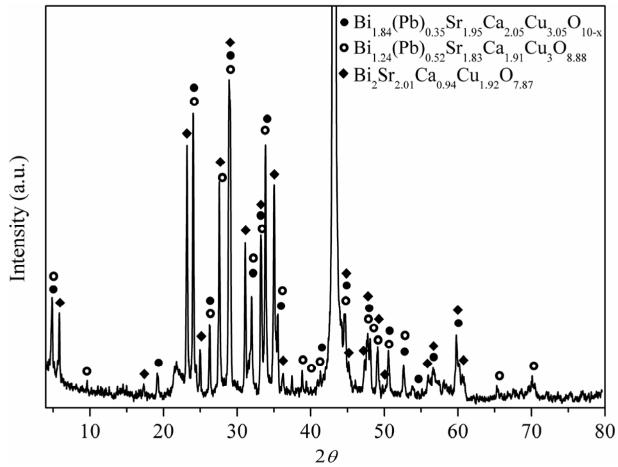

Figure 1. X-Ray diffraction pattern for $Bi_{1.4}Pb_{1.4}Sr_2Ca_2Cu_3O_\delta$/MgO film, prepared following the experimental conditions of sample 2.

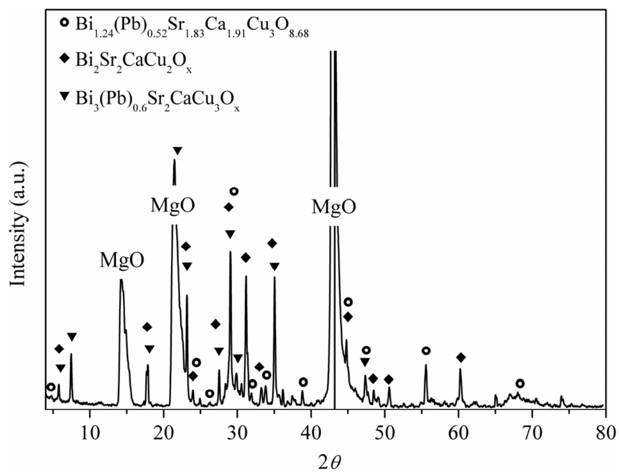

Figure 2. X-Ray diffraction pattern for $Bi_{1.4}Pb_{1.4}Sr_2Ca_2Cu_3O_\delta$/MgO film prepared following the experimental conditions of sample 7.

Table 1. Growth parameter conditions, where ta is the annealing time, ta is the annealing temperature and x is the nominal lead content.

Sample No	Material used to cover the precursor film	t_a [h]	T_a [°C]	x [mole]
1	superconducting pellet	1	840	0.7
2	superconducting pellet	15	850	1.4
3	superconducting pellet	29	860	2.1
4	precursor film	1	850	2.1
5	precursor film	15	860	0.7
6	precursor film	29	840	1.4
7	plate-shaped crystalline MgO	1	860	1.4
8	plate-shaped crystalline MgO	15	840	2.1
9	plate- shaped crystalline MgO	29	850	0.7

between 1 h and 29 h exists. On the other hand, to observe the effect, in the growing of superconductor Bi-based, using different conditions to those above mentioned, **Figures 3** and **4** from films 5 and 9 are shown. From **Figure 3** we can observe that the $Bi_2Sr_{2.01}Ca_{0.94}Cu_{1.92}O_{7.87}$ phase, related to that denominated Bi-2212 phase, was grown using an annealing temperature of 860ºC during 15 h and Pb content of 0.7 mole. With those conditions it was no possible to grow the Bi-2223 phase, because of the effect of annealing temperature, higher than 850ºC, and those one from the Pb content, lower than 1.4 mole, even when the annealing time was established in 15 h.

Figure 4 shows the growing of the $Bi_{1.6}Pb_{0.595}Sr_{2.675}Ca_{2.675}Cu_3O$ phase and a Bi-deficient phase $Bi_{0.33}Pb_{3.4}Sr_{2.6}Ca_{2.3}Cu_2O$, with an annealing temperature of 850ºC during 29 h and Pb content of 0.7 mole.

With those conditions it was no possible to grow the Bi-2223 and Bi-2212 phases, because the annealing time was higher than 15 h and Pb content was lower than 1.4 moles, even when annealing temperature was established at 850ºC. Those results show interdependence between Pb content, annealing temperature and annealing time.

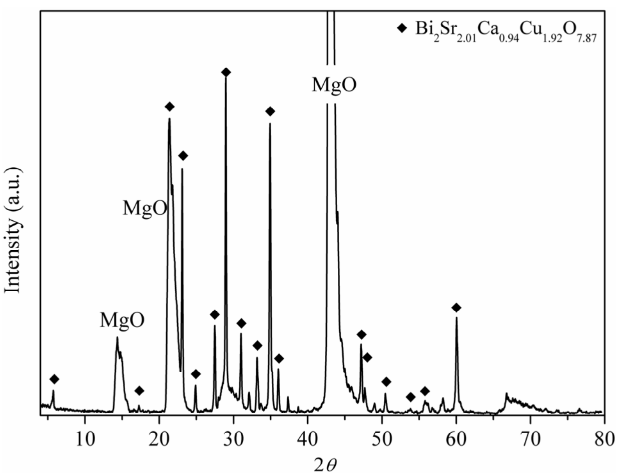

Figure 3. X-Ray diffraction pattern for $Bi_{1.4}Pb_{0.7}Sr_2Ca_2Cu_3O_\delta$/MgO film prepared following the experimental conditions of sample 5.

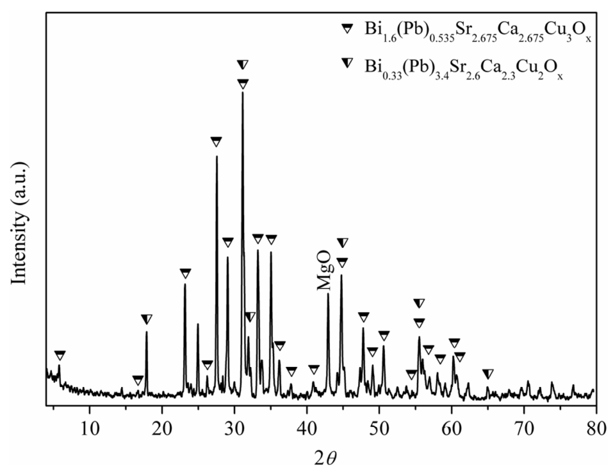

Figure 4. X-Ray diffraction pattern for $Bi_{1.4}Pb_{0.7}Sr_2Ca_2Cu_3O_\delta$/MgO film prepared following the experimental conditions of sample 9.

3.2. Resistance vs. Temperature Dependence

Results of the *R* vs. *T* measurements, from all the superconducting films gave T_{c0} values between 23 and 99 K, are listed in **Table 2**. **Figure 5** shows the electrical behavior for all samples. Most of them show a metallic behavior before the superconducting transition. Samples 2 and 7 gave the highest T_c values of 91 and 99 K, respectively. After thermal treatment, samples 3 and 8 were very thin and it was no possible to measure their T_{c0} values because of missing conductive paths.

Table 2. Results of final pb content (x_f) determined by atomic absorption spectroscopy and the critical temperature values, t_{c0}, of the bi-based films.

Sample	x_f [mole]	T_{c0} [K]
1	0.4	37
2	0.2	91
3	0.3	–
4	2.3	65
5	0.4	23
6	1.3	45
7	1.9	99
8	2.4	–
9	0.8	59

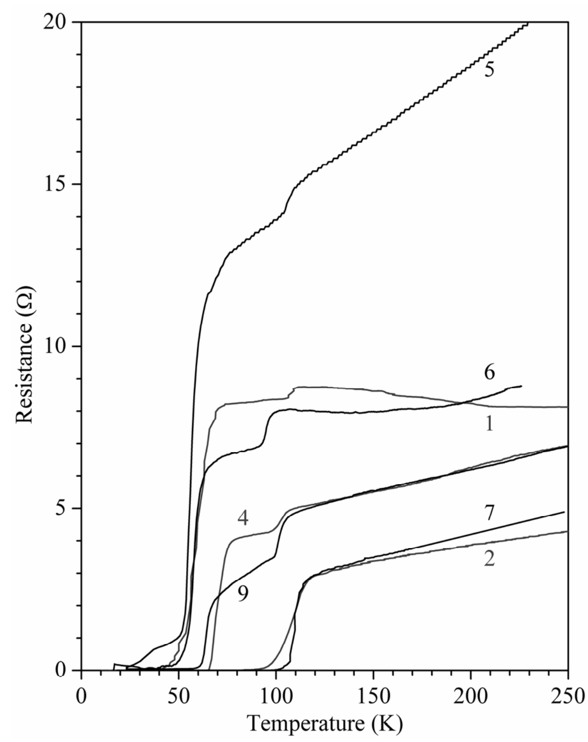

Figure 5. Resistance vs. temperature measurements of the samples no. 1, 2, 4, 5, 6, 7 and 9.

According to X-ray diffraction results and *R* vs. *T* dependence for samples 2 and 7 it is observed that covering material does not have influence in the result. While sample 2 was covered with a superconducting pellet, sample 7 was covered with an MgO substrate. In both films the same electrical behavior was obtained approximately. From these results we can observe that covering the film helps to keep partial vapor pressure of Pb and so avoid its evaporation. Also it was verified that Pb reduces the melting point of the film and therefore high annealing temperatures (860ºC), high annealing times (29 h) and high Pb content cause the evaporation of the material, i. e., the combination of Pb content equal to 2.1 mol, annealing time of 29 h and annealing temperature of 860ºC which are the limit conditions, result in negative form in the superconducting properties of the film.

On the other hand, an initial Pb content of 0.7 moles with a low annealing temperature of 840ºC and an annealing time of 15 h are not sufficient to grow high-T_c superconducting phases and therefore not superconducting electrical behavior in the films is presented.

4. Conclusions

The Pb content necessary in the formation of the high-T_c phases depends on the combination of t_a and T_a. This means that exists an interrelation among Pb content, t_a and T_a. Therefore, the electrical behavior of the films 2 and 7 verifies the interdependence between Pb content, annealing time and annealing temperature. This means that the presence of Pb is necessary to stabilize the high-T_c phase but its content depends on the annealing conditions.

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