ELSEVIER

Thin Solid Films 373 (2000) 122–128

thin solid films

www.elsevier.com/locate/tsf

Bi–Pb–Sr–Ca–Cu–O/MgO superconducting thin films

E. Díaz-Valdés[a,*], M. Jergel[b], C. Falcony-Guajardo[b], F. Morales[c], J. Araujo-Osorio[d]

[a] *Escuela Superior de Física y Matemáticas-I.P.N., Edif 9 UPALM, México D.F. 07738, México*
[b] *Centro de Investigación y Estudios Avanzados-I.P.N., A.P. 14-740, México, D.F. 07000, México*
[c] *Instituto de Investigaciones en Materiales, UNAM, A.P. 70-360, México D.F. 04510, México*
[d] *Escuela Superior de Ingeniería Química e Industrias Extractivas-IPN, Edif. 7 UPALM, México D.F., 07738, México*

Abstract

Bi–Pb–Sr–Ca–Cu–O/MgO thin films were prepared by deposition of an aerosol from aqueous nitrate solutions. To prepare the samples, an experimental design was applied to investigate the influence of nine different variables upon the synthesis of superconducting phases. Within this design, the influence of the chemical composition of the nitrate solutions and the precursor thermal treatment upon formation of the superconducting phases were studied. The T_c values of the samples were used as a quantitative parameter to analyze and optimize various parameters studied in the film preparation. The analysis revealed a significant influence of the Bi and/or the Bi/Pb content as well as that of Cu and the thermal treatment parameters. Results from XRD, SEM, EDS and T_c measurements showed a correlation between the film preparation conditions, the film chemical composition and the formation of superconducting phases. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Superconducting Bi-based films; Film processing; Film properties; Experimental design

1. Introduction

Since the discovery of the bismuth-based superconductors [1,2], a variety of applications of the bulk material [3] as well as thin films [4–8] have been reported. Bi-based films are already used in low current as well as power (transmission lines) applications. Currently, several physical [4–6] and chemical techniques [7,8] are being used for their preparation. It has been found that the nominal composition and thermal treatment parameters such as heating rate, annealing temperature, annealing time, and cooling rate play an important role in the formation of high-T_c phases [8,9]. It is also known that the addition of Pb, together with an appropriate fabrication process, increases the content of high-T_c phases and the thermodynamic stability of these phases [2,6,7]. 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 [5] is also recognized. A cooling rate following the sintering of a sample is another parameter that has been found to affect the growth of the high-T_c phases. It has been reported [4] that by rapid cooling it is possible to grow an almost single-phase 110 K film. Another variable in the processing of superconducting materials is the oxygen content that can be introduced by keeping its partial pressure constant during the thermal treatment, or chemical reaction as in our case. In the BSCCO system, in comparison to the YBCO one, the change in T_c in relation to the oxygen content has been found to be much less dependent [10]. To grow Bi-based superconducting films, different types of monocrystalline substrates such as yttrium stabilized zirconia (YSZ), $SrTiO_3$, BeO, $LaAlO_3$ and/or MgO (001) have been used up to now by various authors. From the point of view of their lattice parameters, thermal expansion coefficients and the best electrical properties of the synthesized Bi-based films, the $SrTiO_3$, $LaAlO_3$ and MgO (001) substrates seem to

* Corresponding author. Tel.: +52-5-729-61-39.
E-mail address: elviadv@esfm.ipn.mx (E. Díaz-Valdés).

0040-6090/00/$ - see front matter
PII: S0040-6090(00)01117-2

be the most suitable ones [4–6,8]. Taking into consideration also the cost of these substrates, we selected MgO (001) for the present experimental work.

When growing Bi-based films, many technological parameters are involved in such a process, influencing the final properties of the synthesized films. In this work we investigated the influence of the most important parameters. The value of each of the investigated parameters may be varied only within a particular interval, limited by its minimum and maximum value. In order to minimize and optimize the number of experiments needed for investigation of the influence of each of these particular factors, we considered for our experimental design only these two values. We presumed that such a change in the investigated parameter depends on a change in value of the rest of the participating factors. Applying a statistical experimental design allowed us not only to learn the importance of individual factors involved in the process, but also to quantify their influence upon the response ($T_{c, on}$ values). The general characteristic of experimental designs of this type is that more than one parameter is changed in each experimental run so as to limit the number of experiments performed (in our particular case we changed 9 parameters at the same time).

The presented experiment consists of 16 trials, with the aim of evaluating nine processing factors affecting the superconducting and physical properties of the films. The effect of the factors at two levels (high and low values inside an interval of the corresponding factor) on the film properties could be efficiently identified using a fractional factorial design 2^{9-5}_{III}, which allowed fast, economical and accurate evaluation of this preparation process depending upon several factors [11,13]. The factors studied here were: Bi, Pb, Sr, Ca, and Cu content; heating time, t_h (from room temperature to annealing temperature); annealing temperature, T_a; annealing time, t_a; and the ambient to which samples were quenched after annealing, Q. The prepared films were characterized structurally, morphologically, chemically, electrically and magnetically in order to evaluate the results of a such statistic experimental design.

2. Experimental

Bi–Pb–Sr–Ca–Cu–O film precursors were prepared by deposition of an aerosol from aqueous nitrate solutions on MgO substrates. Following our experimental design we investigated the influence of nine different variables on the synthesis of high-T_c phases, Table 1. The variation in the factors at two levels (low–high and/or min–max) was as follows: Bi in the mole number $n_{Bi} = 1.65$ and 2.09; Pb in the mole number $n_{Pb} =$ 0.22 and 0.44; Sr in the mole number $n_{Sr} = 1.98$ and 2.42; Ca in the mole number $n_{Ca} = 1.98$ and 2.42; Cu in the mole number $n_{Cu} = 2.75$ and 3.85; heating time $t_h = 0.5$ and 1 h; annealing temperature $T_a = 855$ and 859°C; annealing time $t_a = 10$ and 15 h; and the ambient into which samples were quenched after anneal-

Table 1
Parameters used to prepare Bi–Pb–Sr–Ca–Cu–O films

Trial no.	Parameters for film preparation[a]								
	n_{Bi}	n_{Sr}	n_{Pb}	n_{Cu}	n_{Ca}	T_a (°C)	t_a (h)	t_h (h)	Q
1	1.65	1.98	0.22	2.75	1.98	855	10	0.5	Air
2	2.09	1.98	0.22	2.75	2.42	855	15	1	$N_{2,liq}$
3	1.65	2.42	0.22	2.75	2.42	859	10	1	$N_{2,liq}$
4	2.09	2.42	0.22	2.75	1.98	859	15	0.5	Air
5	1.65	1.98	0.44	2.75	2.42	859	15	0.5	$N_{2,liq}$
6	2.09	1.98	0.44	2.75	1.98	859	10	1	Air
7	1.65	2.42	0.44	2.75	1.98	855	15	1	Air
8	2.09	2.42	0.44	2.75	2.42	855	10	0.5	$N_{2,liq}$
9	1.65	1.98	0.22	3.85	1.98	859	15	1	$N_{2,liq}$
10	2.09	1.98	0.22	3.85	2.42	859	10	0.5	Air
11	1.65	2.42	0.22	3.85	2.42	855	15	0.5	Air
12	2.09	2.42	0.22	3.85	1.98	855	10	1	$N_{2,liq}$
13	1.65	1.98	0.44	3.85	2.42	855	10	1	Air
14	2.09	1.98	0.44	3.85	1.98	855	15	0.5	$N_{2,liq}$
15	1.65	2.42	0.44	3.85	1.98	859	10	0.5	$N_{2,liq}$
16	2.09	2.42	0.44	3.85	2.42	859	15	1	Air
17[b]	1.65	2.42	1.8	3.85	2.42	859	15	2	Air

[a] n_{Bi}, n_{Pb}, n_{Sr}, n_{Ca}, and n_{Cu} are the nominal amount of moles of Bi, Pb, Sr, Ca and Cu elements in the source solution; t_h is the heating time from room temperature to annealing temperature; T_a is the annealing temperature and t_a is the annealing time; and Q is the ambient into which samples were quenched after annealing.

[b] Sample No. 17 was cooled down to the room temperature over a 2-h period.

ing Q = air and liquid nitrogen. To deposit the precursor films, a spray pyrolysis technique [12] was applied using an ultrasonic generator to nebulize an aerosol. Stock solutions of Bi, Pb, Sr, Ca and Cu nitrates were prepared by dissolving appropriate amounts of $Bi(NO_3)_3$, $Pb(NO_3)_2$, $Sr(NO_3)_2$, $Ca(NO_3)_2 \cdot 4H_2O$, and $Cu(NO_3)_2 \cdot 3H_2O$ in deionized water. Solutions of the metal ions in the corresponding nominal composition (Table 1) were obtained by mixing the appropriate volumes of the stock nitrate solutions. Using air as a carrier gas, the nebulized 0.02 M solutions were sprayed over single crystal MgO (001) substrate preheated to 250°C. The distance between the nozzle orifice and the substrate was kept at approximately 5 cm. The resulting precursor films, 5–10 μm thick, were then annealed in a tube-type furnace in air. The thermal treatment parameters for each sample were varied following the experimental design mentioned above. Sixteen various film-processing procedures were performed and the annealed films were then characterized in order to correlate their real properties with the design parameters. In order to verify results from the experimental design we prepared one final modified trial (no. 17, Table 1) in which we used a substantially increased amount of Pb in comparison with the experimental design analysis. The synthesized film structure was studied by X-ray diffraction on a D-500 Siemens diffractometer in the Bragg–Brentano (θ–2θ) geometry, using CuK_α radiation at 30 kV and 20 mA. The surface morphology was examined by using a JEOL model 35 CF scanning electron microscope. Its energy-dispersive spectroscopy (EDS) attachment was used to analyze the chemical composition of the synthesized films. Magnetic moment vs. temperature measurements with a magnetic field parallel and perpendicular to the sample surface were used to determine the critical temperature $T_{c,\ on}$ (onset) values. The T_c values of some samples were also measured by a standard transport current four-point method, with the 1 μV/cm criteria.

3. Results and discussion

As an evaluation parameter of the quality of the prepared films we used the value $T_{c,\ on}$, which in our case means the onset on the measured magnetization curve, Table 2. The hypothesis of the experimental design assumes that the factors in the level that increase the $T_{c,\ average}$ ($T_{c,\ average}$ is calculated as an average of the $T_{c,\ on}$ values in the low and high levels, which are different for each factor and are fixed by the parameters of the experimental design) let us improve the experimental $T_{c,\ on}$ in subsequent trials. The results of the experimental design analysis [13] suggested that, in order to improve the film $T_{c,\ on}$ values obtained in this study, the following values of factors must be used:

Table 2
The critical temperature $T_{c,\ on}$ values obtained from magnetization measurements[a]

Trial No.	$T_{c,\ on}$ (K)
1	85.5
2	88.0
3	77.5
4	82.5
5	84.0
6	85.5
7	88.0
8	–
9	86.0
10	–
11	85.5
12	–
13	87.0
14	–
15	86.0
16	90.0

[a] Samples of trials No. 8, 10, 12 and 14 were not superconducting.

$n_{Bi} = 1.65$; $n_{Pb} = 0.44$; $n_{Sr} = 2.42$; $n_{Ca} = 1.98$; $n_{Cu} = 3.85$; $t_h = 1$ h; $T_a = 859$°C; $t_a = 15$ h; and Q = air, Fig. 1, which increased the $T_{c,\ average}$ values. In order to improve the $T_{c,\ on}$ values a trial numbered as 17, Table 1, was prepared and the results are also reported here.

The X-ray patterns of the films prepared following the experimental conditions nos. 1, 11, and 16, Fig. 2, show increased amount of two high T_c superconducting phases, namely $Bi_2Sr_2CaCu_2O_8$ (Bi-2212 phase) and $Bi_2Sr_2Ca_2Cu_3O_x$ (Bi-2223 phase) with the Bi content constant at its low level. The thermal treatment parameters varied in this case according to experimen-

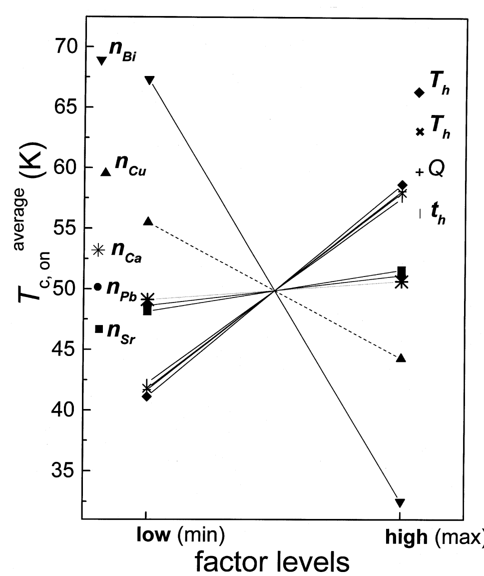

Fig. 1. Influence of parameters studied for two levels (min–max) of the fractional factorial experimental design 2^{9-5}_{III}. Left points in each line represent the minimum values used, and the right ones represent the maximum values.

tal conditions nos. 1, 11, and 16. In Fig. 2a, trial no. 1, the presence of the Bi-2212 phase can be observed. It seems that the nominal composition of the solution conditions $Bi_{1.65}Pb_{0.22}Sr_{1.98}Ca_{1.98}Cu_{2.75}O_x$ and thermal treatment conditions of $t_h = 30$ min, $T_a = 855°C$, $t_a = 10$ h followed by quenching in air are suitable for growing a film with an elevated amount of the Bi-2212 phase. Fig. 2b, trial no. 11, shows the presence of both, Bi-2212 and Bi-2223 phases. An increase in the Cu content from $n_{Cu} = 2.5$ to $n_{Cu} = 3.5$ and an annealing time from 10 to 15 h enables a growth of the Bi-2223 phase. The X-ray pattern Fig. 2c, trial no. 16, shows the presence of the Bi-2223 and (Bi-Pb)-2223 phases obtained when the annealing temperature and Cu cation content increase from 855 to 859°C and/or from 2.75 to 3.85, respectively. We can see that annealing parameters and Cu content at their maximum levels and Bi content at its minimum level allows growth of the Bi-2223 phases. These results show that when the Bi content is used at its minimum value, i.e. $n_{Bi} = 1.6$, and the thermal treatment is also used at its maximum value, besides the 2212 phase, the initial growth of the 2223 phase may also be observed. On the other hand, the X-ray pattern in Fig. 3 shows a negative influence of the high level of Bi content and low level of the thermal treatment parameters on formation of the superconducting phases. Fig. 3a shows the X-ray pattern of the film of trial no. 10, where we can see that Bi with a cation content of 2.09 (high level), annealing time of 10 h (low level), annealing temperature of 859°C (high level) and heating time of 0.5 h (low level), produce an oriented Bi-2201 phase (not superconduct-

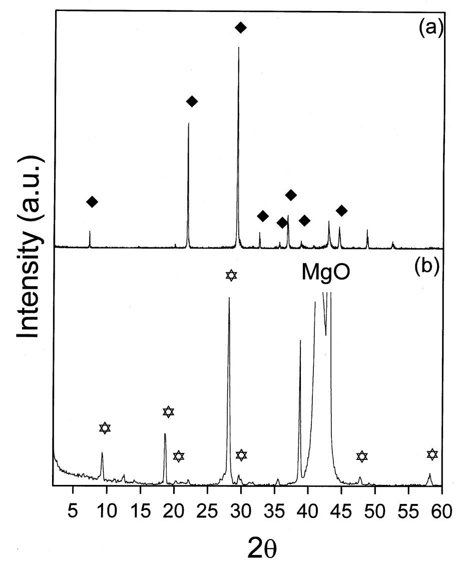

Fig. 3. X-Ray diffraction patterns for Bi–Pb–Sr–Ca–Cu–O/MgO films prepared following the experimental conditions of trial nos.: 10, (a); and 14, (b) Table 1. The detected phases are ◆, $Bi_2Sr_2CuO_6$ and ☆ Bi_2SrO_4.

ing above 10 K). Fig. 3b shows the X-ray pattern for the film of trial no. 14, where we can see the presence of the Bi_2SrO_4 non-superconducting phase obtained when the annealing temperature is reduced to 855°C and the Bi cation content is 2.09. The XRD measurements show both the positive and negative effects of the initial nominal composition of the film, mainly that of Bi content at the low level and Cu at the high level together with the combination of annealing parameters. Apparently an important interaction between the Bi content and the film heat treatment conditions

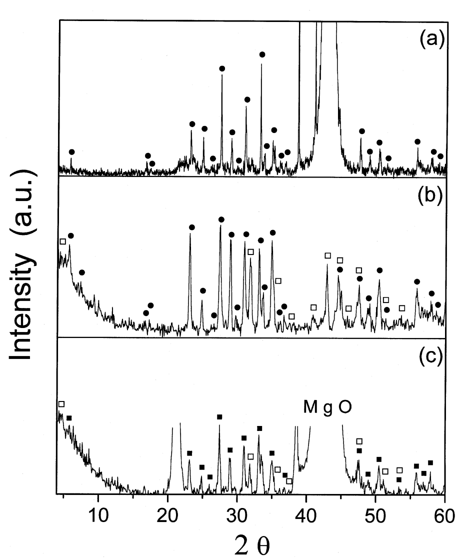

Fig. 2. X-Ray diffraction patterns for Bi–Pb–Sr–Ca–Cu–O/MgO films prepared following the experimental conditions of trial nos.: 1, (a); 11, (b); and 16, (c) Table 1. The detected phases are: ●, $Bi_2Sr_2CaCu_2O_8$; □, $Bi_2Sr_2Ca_2Cu_3O_x$; and ■, $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_x$.

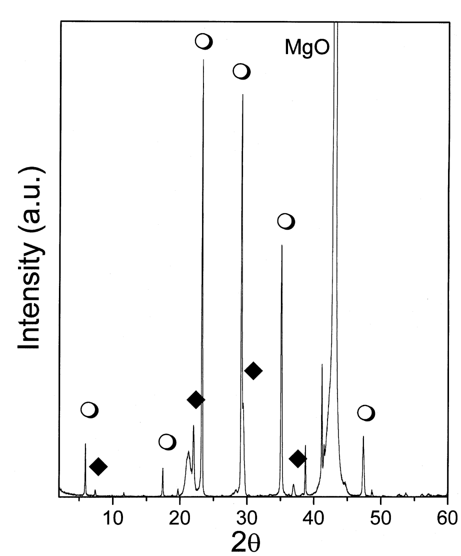

Fig. 4. X-Ray diffraction pattern of Bi–Pb–Sr–Ca–Cu–O/MgO film prepared following the experimental conditions of trial no. 17 Table 1. The detected phases are: ○, $Bi_2S_2Ca_2Cu_4O_x$, and ◆, $Bi_2Sr_2CuO_6$.

exists, since the formation of superconducting phases depends upon Bi content at the low level and annealing conditions at the high level. In the opposite case, a high Bi content and low annealing conditions produce loss of the Bi-2212 and Bi-2223 phases. These results are in agreement with those reported in references [5,14,15]. Fig. 4 shows the X-ray pattern of the film prepared following trial no. 17, which represents the best preparation conditions studied here, giving the highest T_c value. Formation of the 00l oriented Bi-2224 phase may also be seen.

Fig. 5a shows a surface morphology obtained with backscattered electrons from the film of trial no. 11, which consists mainly of plate-like crystal grains oriented parallel with the film surface, with the real film composition $Bi_{1.65}Sr_{1.65}Ca_{1.3}Cu_{2.8}O_x$. Irregular dark particles of the $SrCaCu_4$ composition may also be observed. All the films presented Pb deficiency due to its partial evaporation during annealing. Fig. 5b shows the film surface morphology (obtained by means of backscattered electrons) of the film of trial no. 16, which also consists mainly of plate-like grains oriented parallel to the film surface with the real composition $Bi_{1.65}Pb_{0.08}Sr_{1.54}Ca_{1.73}Cu_{1.56}O_x$. The irregular dark particles consist of a Sr–Ca–Cu–O phase rich in Sr. From those pictures we can observe that both annealing time and temperature have a pronounced influence on the particle size. The size of the grains increases with annealing time and temperature [12]. However, the EDS analyses suggest a strong loss of the Pb component in the films, which meant it was necessary to increase the initial amount of Pb to show its effect upon the growth of superconducting phases in trial no. 17. Fig. 6a shows the surface morphology obtained with backscattered electrons from the film of trial no. 10. We can see dark particles of Cu arising from melted material of composition $Bi_2Pb_{0.15}Sr_{1.4}Ca_{0.7}Cu_{1.4}O_x$. Fig. 6b reveals the surface morphology obtained also by means of backscattered electrons from the film of trial no. 14. Here we may observe round dark particles of the composition $Bi_{1.2}Sr_{1.4}Ca_{0.4}Cu_{0.1}O_x$ arising from the well-oriented plate-like grains of the composition $Bi_2Sr_1Ca_{0.4}Cu_{0.1}O_x$. The SEM investigations allowed us to observe that the conditions where Bi is maintained at cation content 1.65, in combination with the annealing conditions kept at their high level, enable the growth of plate-like grains oriented parallel with the substrate surface. According to the XRD analysis, the grain phase composition correspond mainly to the Bi-2212 and Bi-2223 phases which is also in agreement with the EDS analysis. When maximum values of annealing parameters and the maximum Bi content are used, the material is melted and phases without the presence of calcium are formed. Particles then appear rich in strontium and calcium without the presence of copper.

Fig. 5. Surface morphology obtained with backscattered electrons for Bi–Pb–Sr–Ca–Cu–O/MgO films prepared following the experimental conditions of trial nos. 11, (a) and 16, (b) Table 1.

Fig. 7 shows the magnetic moment vs. temperature dependence of several films prepared following experi-

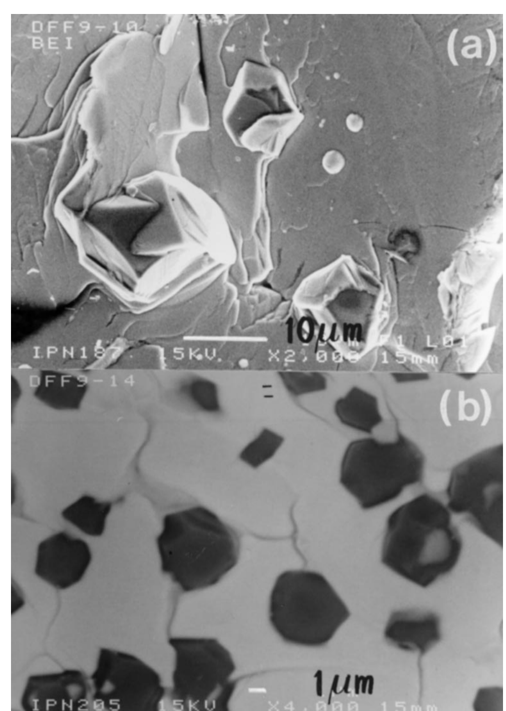

Fig. 6. Surface morphology obtained with backscattered electrons for Bi–Pb–Sr–Ca–Cu–O/MgO films prepared following the experimental conditions of trial nos. 10, (a) and 14, (b) Table 1.

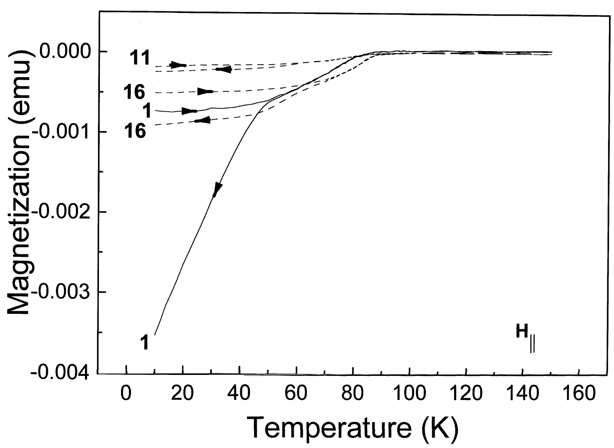

Fig. 7. The magnetization vs. temperature dependence for Bi–Pb–Sr–Ca–Cu–O/MgO films prepared following the experimental conditions of trial nos. 1, 11 and 16. The magnetic field was oriented parallel to the film surface. The intensity of magnetic field was 100 Oe (---) and 1000 Oe (—).

mental conditions nos. 1, 11 and 16, obtained with the magnetic field parallel to the film surface. All the films prepared with Bi content at its low level were superconducting. Films prepared with the maximum Bi content either did not present any superconducting transition, or only presented very low $T_{c,\ on}$ values. The magnetization curves of all the measured films were similar. Results of the $T_{c,\ on}$ measurements show that, in order to obtain higher $T_{c,\ on}$ values, it is necessary to keep the Bi content at its minimum value, $n_{Bi} = 1.65$, and the heat processing parameters at their maximum values, i.e. $T_a = 859°C$ and $t_a = 15$ h.

Fig. 8 shows the resistance vs. temperature dependence of the films of trial nos. 11 and 17, Table 1. Here

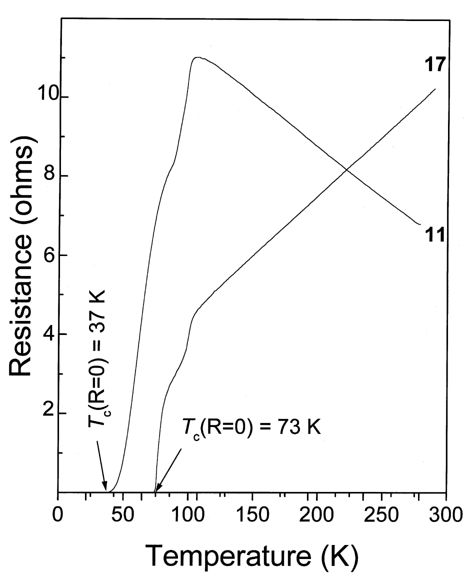

Fig. 8. The resistance vs. temperature dependence for Bi–Pb–Sr–Ca–Cu–O/MgO films prepared following the experimental conditions of trial nos. 11 and 17 Table 1.

we observe semiconducting behavior for film no. 11, with two transitions at 96 and 68 K, and T_c ($R = 0$) = 37 K. The dependence for the film from trial no. 17, prepared with a substantially increased amount of lead, is also shown in Fig. 8. Here we can see a metallic behavior, with two transitions at 105 and 84 K, and T_c ($R = 0$) = 73 K. Results from Fig. 8 show the usefulness of our experimental procedure and its systematic approach, with the aim of obtaining superconducting samples with higher critical temperature T_c values.

4. Conclusion

Films of 5–10 μm in thickness were prepared by a spray pyrolysis technique according to a fractional factorial experimental design. Results of the analyses of the experimental design, and those obtained from characterizations (XRD, SEM, EDS and the critical temperature value measurements) of the films, showed that the variables with the highest influence on the growth of high-T_c superconducting phases are Bi content, annealing time and temperature, and the quenching ambient. The results suggest the use of the value of 1.65 (low level) as a mole content of Bi, thermal treatment conditions at their high level values, i.e. 1 h, 859°C, 15 h, and air as a quenching ambient for t_h, T_a, t_a and Q respectively, to obtain superconducting BSCCO films with improved properties. On the other hand, we can see that a change in the Sr and Ca content have a lesser influence on improving the superconducting properties when their mole content is between 1.98 and 2.42. An evident loss of Pb was observed during all of the experimental work, caused by its partial evaporation. The most significant improvement in T_c values was obtained by utilizing the following conditions:

- Nominal contents of $n_{Bi} = 1.65$, $n_{Cu} = 3.85$, $n_{Sr} = 2.42$, $n_{Ca} = 2.42$, with a substantial increase in the Pb content from the nominal value $n_{Pb} = 0.44$ to $n_{Pb} = 1.8$ in deposited precursor films.
- Annealing carried out with heating time $t_h = 2$ h, annealing temperature $T_a = 859°C$, and an annealing time of $t_a = 15$ h.
- Cooling in air to room temperature for 2 h.

Acknowledgements

The authors acknowledge the technical assistance of J. García-Coronel and M. Guerrero-Cruz. The work was supported by CEGEPI-IPN Project No. 980250.

References

[1] H. Maeda, Y. Tanaka, M. Fukutomi, T Asano, Jpn. J. Appl. Phys. 27 (1988) L209–L210.
[2] M. Takano, J. Takada, K. Oda et al., Jpn. J. Appl. Phys. 27 (1988) L1041–L1043.

[3] E. Díaz-Valdés, G. Pacheco-Malagón, G. Contreras-Puente et al., Mater. Chem. Phys. 36 (1993) 64–67.
[4] K. Ikeda, K. Gotoh, M. Ihara, M. Ozeki, Jpn. J. Appl. Phys. 28 (1989) L650–L652.
[5] K. Ohbayashi, M. Anma, Y. Takai, H. Hayakawa, Jpn. J. Appl. Phys. 29 (1990) L2049.
[6] W. Kula, R. Sobolewski, J. Górecka, S.J. Lewandowski, J. Appl. Phys. 70 (1991) 3171.
[7] N. Takahashi, A. Koikitu, H. Seki, Y. Kamioka, J. Cryst. Growth 144 (1994) 48.
[8] H. Nobumasa, K. Simizu, Y. Kitano, T. Kawai, Jpn. J. Appl. Phys. 27 (1988) L1669.
[9] H.S. Koo, G.C. Tu, J.J. Chu, W.H. Lee, P.T. Wu, J. Mater. Sci. Lett. 9 (1990) 1326–1328.
[10] R.G. Buckley, J.L. Tallon, I.W.M. Brown et al., Physica C 156 (1988) 629.
[11] D.C. Montgomery, Design and Analysis of Experiments, 1st ed., Wiley, New York, 1976, pp. 235–239.
[12] M. Jergel, F. Hanic, V. Strbik et al., Supercond. Sci. Technol. 5 (1992) 663.
[13] E. Díaz, et. al. Application of the fractional factorial experimental design in the preparation of superconducting thin films, in press.
[14] H.M. Hsu, I. Yee, J. Deluca, C. Hilbert, R.F. Miracky, L.N. Smith, Appl. Phys. Lett. 54 (1989) 957.
[15] H.S. Koo, G.C. Tu, J.J. Chu, W.H. Lee, P.T. Wu, J. Mater. Sci. Lett. 9 (1990) 1326.