

Journal of Crystal Growth 210 (2000) 587-594

JOURNAL OF CRYSTAL GROWTH

www.elsevier.nl/locate/jcrysgro

Growth of BiSrCaCuO thin films by MOCVD

Josef Stejskal^a, Jindřich Leitner^{b,*}, David Sedmidubský^a, Miloš Nevřiva^a, Přemysl Beran^a, Aleš Strejc^a

^aDepartment of Inorganic Chemistry, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic ^bDepartment of Solid State Engineering, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic

> Received 29 July 1999; accepted 30 November 1999 Communicated by L.F. Schneemeyer

Abstract

Thermodynamic analysis of the system Bi-Sr-Ca-Cu-O-C-H-Ar using the Gibbs energy minimization method was performed to propose feasible deposition conditions for the growth of superconducting Bi-2212 films. The results show that the films containing Bi-2212 can be prepared at temperatures above 1000 K under reduced pressure with the input ratio Bi : Sr : Ca : Cu close to 2:2:1:2. The growth experiments were carried out in a cold-wall RF-heated quartz reactor at temperatures of 800 and 850°C and a total pressure of 1 kPa. 2,2,6,6-tetramethyl-3,5-heptanedionates of Cu, Ca and Sr and triphenylbismuth were used as metal precursors. The films were characterized by X-ray diffraction, electron microprobe analysis and scanning electron microscopy. The highest critical temperature determined by measuring the AC magnetic response was 71 K. © 2000 Elsevier Science B.V. All rights reserved.

PACS: 74.72.Hs; 74.76.Bz; 74.25.Bt; 85.15.Gh

Keywords: Superconductors; Thin films; MOCVD; Thermodynamics

1. Introduction

The study of preparation methods as well as the properties of high- T_c oxide superconductors remains a challenging problem of material investigation in the field of inorganic nonmetallic materials. The Bi-Sr-Ca-Cu-O system (BSCCO) contains three reported superconducting phases, namely Bi_{2+x}Sr_{2-y}CuO_z (Bi-2201, $T_c \approx 20$ K), Bi₂Sr₂Ca-Cu₂O_{8+x} (Bi-2212, $T_c \approx 85$ K) and Bi₂Sr₂Ca₂-

Cu₃O_{10+x} (Bi-2223, $T_c \approx 110$ K). Recently, metalorganic chemical vapor deposition (MOCVD) has been successfully used to grow thin films of the Bi-2212 phase with $T_c > 80$ K and Bi-2223 with $T_c \approx 100$ K [1–4]. Volatile β -diketonate complexes of Cu, Ca and Sr or their fluorinated derivatives and triphenylbismuth are typically employed as the metal precursors.

Equilibrium thermodynamic calculations represent a very useful tool for simulating the MOCVD process and predicting suitable deposition conditions [5–7]. Such calculations using the Gibbs energy minimization technique have been performed for MOCVD of the Bi-2212 phase [8]. In this study, several simplifications have been adopted as

^{*}Corresponding author. Tel.: + 420-2-2435-5156; fax: + 420-2-2431-0337.

E-mail address: leitnerj@vscht.cz (J. Leitner)

the thermodynamic data for complex oxides existing in the BSCCO system were unavailable.

The first part of this paper reports results of thermodynamic analysis of the system Bi-Sr-Ca-Cu-O-C-H-Ar. Contrary to the earlier study [8], 22 mixed oxides (binary, ternary and quaternary), for which the thermodynamic data were either taken from recent literature or estimated, were included in our calculations. Based on these results appropriate deposition conditions for the Bi-2212 phase growth were proposed. The deposition of the BSCCO thin layers by MOCVD using the 2,2,6,6tetramethyl-3,5-heptanedionates of Cu, Ca and Sr and triphenylbismuth and characterization of these films is described in the second part of the paper.

2. Thermodynamic calculations

A general method [9,10] based on the minimization of the total Gibbs energy of the system on a set of points satisfying the material balance conditions was used for the calculation of equilibrium composition of the Bi-Sr-Ca-Cu-O-C-H-Ar system. 43 gaseous species and 37 stoichiometric solid compounds were included in the calculations (see Table 1). In the case of ternary and quaternary oxides, the values of the heat of formation (ΔH_{ox}) and the entropy of formation (ΔS_{ox}) from simple oxides were estimated earlier [11,12]. With respect to the investigated range of conditions mentioned below, no liquid phase was considered.

The calculations were performed for temperatures ranging from 600 to 850°C, at atmospheric or reduced total pressures, for various initial compositions of the gaseous phase. 2,2,6,6-tetramethyl-3,5-heptanedionates of Sr, Ca and Cu (Me(thd)₂, Me = Sr, Ca and Cu, thd = $C_{11}H_{19}O_2$) and triphenylbismuth $(Bi(ph)_3, ph = C_6H_5)$ were taken as metal elements precursors. Pure O_2 or a mixture of O_2 + Ar were considered as the source of oxygen. Input ratio $O_2/\Sigma Me$, $O_2/\Sigma Me = n^{\circ}(O_2)/$ $[n^{\circ}(\text{Bi}(\text{ph})_3) + n^{\circ}(\text{Sr}(\text{thd})_2) + n^{\circ}(\text{Ca}(\text{thd})_2) + n^{\circ}(\text{Cu})$ $(\text{thd})_2$, was varied in the range of $10^2 - 10^4$. Because the metalorganic compounds are unstable at elevated temperatures and no relevant thermodynamic data exist, they were not considered in the calculations. Instead, a combination of gaseous ele-

Table 1

Substances included in the calculations and sources of thermodynamic data

Gasaous species	
Bi Bi Bi Bi D Bi O Bi O	F137
$B_1, B_2, B_3, B_4, B_20, B_20_2, B_20_3, B_10, B_10$	[15]
Віз 04, Ві4 06, Віо	F1/J
$\sum_{n=1}^{n} \sum_{n=1}^{n} \sum_{n=1}^{n} \sum_{i=1}^{n} \sum_{n=1}^{n} \sum_{i=1}^{n} \sum_{i$	[14]
$S_1, S_1(0, S_1(0, 0)_2, S_1(0, 0)_2)$	[13]
	[10]
SIH	[1/]
$Ca, Ca_2, CaO, Ca(OH)_2, CaOH$	[15]
Сан	[1/]
Cu, Cu_2, CuH, CuO	
$O, O_2, H, H_2, H_2O, C, CH_4, C_2H_6, C_2H_4,$	[14]
C_2H_2 , CO , CO_2	
$CH_3OH, CH_2O, CHOOH$	[17]
Ar	[15]
Solid substances	
Bi ₂ O ₃	[13]
SrO	[15,18]
SrO ₂	[14]
CaO	[19]
CaO ₂	[14]
Cu ₂ O, CuO	[15]
Bi_2SrO_4 , $Bi_2Sr_2O_5$, $Bi_2Sr_3O_6$, $Bi_4Sr_6O_{15}$,	[20]
$Bi_2Sr_6O_{11}$	
$Bi_{14}Ca_5O_{26}$, Bi_2CaO_4 , $Bi_6Ca_4O_{13}$, $Bi_2Ca_2O_5$	[21]
Bi ₂ CuO ₄	[22]
Sr_2CuO_3 , $SrCuO_2$, $Sr_{14}Cu_{24}O_{41}$, $SrCu_2O_2$	[23]
Ca_2CuO_3 , $Ca_{0.833}CuO_{1.93}$, $CaCu_2O_3$	[24]
Bi ₂ Sr ₂ CuO ₆ (Bi-2201), Bi ₂ Sr ₃ Cu ₂ O ₈ ,	[11,12]
Bi ₄ Sr ₈ Cu ₅ O ₁₉	
Bi ₂ Sr ₂ CaCu ₂ O ₈ (Bi-2212), Bi ₂ Sr ₂ Ca ₂ Cu ₃ O ₁₀	[11,12]
(Bi-2223)	
C, SrC ₂ , SrCO ₃ , SrH ₂ , CaC ₂ , CaCO ₃ , CaH ₂	[14]

ments in relevant stoichiometry was used as the input gaseous mixture.

The oxygen nonstoichiometry of some mixed oxides as well as the existence of various solid solutions were neglected in the calculations. This is the principal simplification of the thermodynamic description of the system under investigation, and can introduce some uncertainty into the calculated equilibrium composition.

3. Experimental procedure

The MOCVD apparatus which was used for growth experiments has been described in detail in

Ref. [25]. This apparatus consists of evaporators for metalorganic precursors, a horizontal RFheated cold-wall quartz reactor, and a vacuum system. The stainless-steel evaporators were placed in accurately temperature-controlled furnaces $(+0.2^{\circ}C)$. The individual precursors Bi(ph)₃, $Sr(thd)_2$, $Ca(thd)_2$ and $Cu(thd)_2$ were heated at temperatures 135-140, 215-220, 245-250, and 120–130°C, respectively. A carrier gas (Ar) flow rate of 25 cm³/min was used to transport the metal sources. All metalorganic feed lines were wrapped in a heating tape and could be heated up to 260° C to avoid undesirable condensation. The metalorganic vapors and argon carrier gas were mixed with oxygen (500 cm^3/min) prior to entering the deposition zone of the reactor. The ratio $O_2/\Sigma Me$ in the input gas stream was varied in the range of $(3-8) \times 10^4$.

Mechanically polished $SrTiO_3(1\ 0\ 0)$ and $Y_3Ga_5O_{12}(1\ 0\ 0)$ single-crystal substrates $(10 \times 10 \times 0.5 \text{ mm})$ were degreased with acetone and isopropanol and placed on the inconel alloy susceptor. The layers were deposited at a substrate temperature of 800–850°C under a total pressure of 1 kPa and an oxygen partial pressure of 0.8 kPa. The substrate temperature was controlled with an accuracy of $\pm 3^{\circ}$ C and monitored by a Pt/Pt-Rh thermocouple. After the growth process, all MO sources were switched to the vent line and samples were cooled to room temperature without argon

and oxygen supply. The typical thickness of the prepared films was 10^{-1} - 10^{-2} µm, as estimated from the weight of the deposited laver on the substrate and considering the approximate density 6.5 g cm^{-3} of the grown Bi-Sr-Ca-Cu-O films. The deposition rate was found to be around 10^{-3} - 10^{-4} µm min⁻¹. BiSrCaCuO films were characterized by X-ray diffraction (XRD) using Cu K_{α} radiation. The chemical composition of several selected samples was analyzed by electron microprobe analysis (EMA) and the surface morphology was examined by scanning electron microscopy. The critical temperature, $T_{\rm C}$, and the broadness of the transition to superconducting state were determined by measuring the AC magnetic response in the temperature range between 9 and 150 K. Both the real and imaginary parts of the signal were recorded.

4. Results and discussion

The calculated equilibrium-phase assemblages for various conditions are given in Tables 2 and 3. The following conclusions can be drawn from the calculated results:

• Bi-2223 is not stable under the given conditions. This follows from the expression for the Gibbs

Table 2

Equilibrium phase composition of the system Bi-Sr-Ca-Cu-O-C-H-Ar($\Sigma Me = 7 \times 10^{-5}$ mol, Bi : Sr : Ca : Cu = 2 : 2 : 1 : 2, n°(Ar) = n°(O₂), p = 1 atm)

$O_2/\Sigma Me$	600°C	650°C	700°C	750°C	800°C	850°C
10 ²	CaCO ₃ CuO	CaCO ₃ CuO	CuO SrCO2	CuO SrCO2	CuO SrCO2	CuO SrCO2
	SrCO ₃ Bi ₂ CuO ₄	$\begin{array}{c} SrCO_3\\ Bi_{14}Ca_5O_{26} \end{array}$	$\begin{array}{c} Bi_{14}Ca_5O_{26}\\ Bi_6Ca_4O_{13} \end{array}$	$\begin{array}{c} \operatorname{Bi}_{14}\operatorname{Ca}_5\operatorname{O}_{26}\\ \operatorname{Bi}_6\operatorname{Ca}_4\operatorname{O}_{13} \end{array}$	$\begin{array}{c} \operatorname{Bi}_{14}\operatorname{Ca}_5\operatorname{O}_{26}\\ \operatorname{Bi}_6\operatorname{Ca}_4\operatorname{O}_{13} \end{array}$	Bi_2SrO_4 $Bi_6Ca_4O_{13}$
10 ³	$CuO \\ SrCO_3 \\ Bi_{14}Ca_5O_{26} \\ Bi_6Ca_4O_{13} \\ \end{cases}$	$CuO \\ SrCO_3 \\ Bi_{14}Ca_5O_{26} \\ Bi_6Ca_4O_{13} \\$	$CuO \\SrCO_3 \\Bi_{14}Ca_5O_{26} \\Bi_6Ca_4O_{13}$	$CuO \\ SrCO_3 \\ Bi_2SrO_4 \\ Bi_6Ca_4O_{13} \\$	$\begin{array}{c} CuO\\ SrCO_3\\ Bi_2SrO_4\\ Bi_2Ca_2O_5 \end{array}$	CaO Bi ₂ Sr ₂ O ₅ Sr ₁₄ Cu ₂₄ O ₄₁ Bi-2212
104	$CuO \\ SrCO_3 \\ Bi_{14}Ca_5O_{26} \\ Bi_6Ca_4O_{13} \\ \end{cases}$	$CuO \\ SrCO_3 \\ Bi_2SrO_4 \\ Bi_6Ca_4O_{13} \\$	$CuO \\ SrCO_3 \\ Bi_2SrO_4 \\ Bi_2Ca_2O_5 \\$	$\begin{array}{c} Bi_2SrO_4\\ Bi_2Sr_2O_5\\ Sr_{14}Cu_{24}O_{41}\\ Ca_2CuO_3 \end{array}$	$\begin{array}{c} Bi_{2}Sr_{2}O_{5}\\ Sr_{14}Cu_{24}O_{41}\\ Ca_{2}CuO_{3}\\ \textbf{Bi-2212}\end{array}$	CaO Bi ₂ Sr ₂ O ₅ Sr ₁₄ Cu ₂₄ O ₄₁ Bi-2212

Table 3

$O_2/\Sigma Me$	600°C	650°C	700°C	750°C	800°C	850°C
10 ²	CuO	CuO	CuO	$Bi_2Sr_2O_5$	Bi ₂ Sr ₂ O ₅	CaO
	SrCO ₃	SrCO ₃	SrCO ₃	$Sr_{14}Cu_{24}O_{41}$	SrCuO ₂	$Bi_2Sr_2O_5$
	$Bi_{14}Ca_5O_{26}$	Bi2SrO4	Bi_2SrO_4	Ca_2CuO_3	Ca_2CuO_3	SrCuO ₂
	Bi ₆ Ca ₄ O ₁₃	Bi ₆ Ca ₄ O ₁₃	$Bi_2Ca_2O_5$	Bi-2212	Bi-2212	Bi-2212
10 ³	CuO	SrCO ₃	$Bi_2Sr_2O_5$	$Bi_2Sr_2O_5$	$Bi_2Sr_2O_5$	CaO
	SrCO ₃	$Bi_2Sr_2O_5$	$Sr_{14}Cu_{24}O_{41}$	$Sr_{14}Cu_{24}O_{41}$	SrCuO ₂	$Bi_2Sr_2O_5$
	Bi ₂ SrO ₄	Ca_2CuO_3	Ca_2CuO_3	Ca_2CuO_3	Ca_2CuO_3	SrCuO ₂
	Bi ₂ Ca ₂ O ₅	CaCu ₂ O ₃	$CaCu_2O_3$	Bi-2212	Bi-2212	Bi-2212
104	CuO	$Bi_2Sr_2O_5$	$Bi_2Sr_2O_5$	$Bi_2Sr_2O_5$	Bi ₂ Sr ₂ O ₅	CaO
	Bi ₂ Sr ₂ O ₅	$Sr_{14}Cu_{24}O_{41}$	$Sr_{14}Cu_{24}O_{41}$	$Sr_{14}Cu_{24}O_{41}$	SrCuO ₂	$Bi_2Sr_2O_5$
	$Sr_{14}Cu_{24}O_{41}$	Ca_2CuO_3	Ca_2CuO_3	Ca_2CuO_3	Ca_2CuO_3	SrCuO ₂
	$Ca_{0.83}CuO_{1.9}$	$CaCu_2O_3$	$CaCu_2O_3$	Bi-2212	Bi-2212	Bi-2212

Equilibrium phase composition of the system Bi-Sr-Ca-Cu-O-C-H-Ar ($\Sigma Me = 7 \times 10^{-5}$ mol, Bi : Sr : Ca : Cu = 2 : 2 : 1 : 2, n°(Ar) = n°(O₂), p = 0.01 atm)

energy of the reaction (R1)

$$Bi-2223 = Bi-2212 + \frac{1}{3}Ca_2CuO_3$$

$$+ \frac{1}{3} Ca Cu_2 O_3. \tag{R1}$$

 $\Delta G_1 = -9800 + 2.2T$, and $\Delta G_1 < 0$ in the temperature range of 873–1123 K (600–850°C). Consequently, Bi-2223 is thermodynamically unstable with respect to the set of phases Bi-2212, Ca₂CuO₃ and CaCu₂O₃.

• Bi-2212 can be formed at higher temperatures, reduced pressure and a high input ratio of $O_2/\Sigma Me$. This phase is stable only at temperatures above approximately 1000 K (727°C) as the Gibbs energy of the reaction (R2)

$$Bi-2212 = Bi_2Sr_2O_5 + CaCu_2O_3.$$
(R2)

 $\Delta G_2 = -22500 + 22.5T$, and $\Delta G_2 < 0$ for temperatures T < 1000 K. So Bi-2212 is not stable with respect to the Bi₂Sr₂O₅ and CaCu₂O₃ phases below this temperature.

Bi-2201 (Bi_{2+x}Sr_{2-y}CuO_z), which was considered as strictly stoichiometric phase (Bi₂Sr₂CuO₆), cannot be predicted by equilibrium calculations. The Gibbs energy of the reaction (R3)

$$Bi_2Sr_2CuO_6 = Bi_2Sr_2O_5 + CuO$$
(R3)

 $\Delta G_3 = -64300 + 20.7T$, and $\Delta G_3 < 0$ in the temperature range of 873–1173 K (600–850°C). Thus Bi₂Sr₂CuO₆ is not stable with respect to the combination of Bi₂Sr₂O₅ and CuO.

The calculated results show that the input ratio of Bi : Sr : Ca : Cu close to 2 : 2 : 1 : 2 is suitable for the deposition of Bi-2212. Bi-2212 represents the major phase at these condition and the equilibrium amounts of accompanying phases are insignificant. Adjusting the input metal ratio to 2 : 2 : 2 : 3 results in the formation of Bi-2212 phase, too.

Table 4 summarizes the deposition conditions of BiSrCaCuO thin films and their phase composition determined by XRD. The precursor flow rates (µmol/min) were calculated from the decrease of the precursor mass during the experiment. Congruent precursors evaporation was assumed. Figs. 1 and 2 show X-ray diffraction patterns of pure Bi-2201 and Bi-2212 phases, respectively. X-ray diffraction patterns of a mixture of Bi-2212 and Bi-2223 are given in Fig. 3. Surface morphology of the deposited layer (sample No. 45) is shown in Fig. 4. The AC magnetic response measured on sample No. 64 as a function of temperature is shown in Fig. 5. The following conclusions can be drawn from experimental results:

• In general, the surface of the grown films are smooth. In some cases, droplets or grains of

Table 4

Deposition condition of BiSrCaCuO thin films and their phase composition determined by XRD (total pressure in reactor 1 kPa, oxygen partial pressure 0.8 kPa)^a

Run no.	Flow rates (µmol/min)				Metal ratio	Substrate	Substrate	Solid phase
	Bi(ph)3	$Sr(thd)_2$	Ca(thd) ₂	Cu(thd) ₂	bi . Si . Ca . Cu		temperature (°C)	composition (ARD)
40	0.68	0.95	0.64	0.86	2:2.8:1.9:2.5	$Y_3Ga_5O_{12}$	800	2201
42	0.78	1.02	2.07	1.21	2:2.3:5.3:3.1	SrTiO ₃	800	2201
44	0.78	1.15	0.44	1.06	2:2.9:1.1:2.7	$Y_3Ga_5O_{12}$	850	2201
45	0.99	1.05	0.36	0.87	2:2.1:0.7:1.8	$Y_3Ga_5O_{12}$ SrTiO ₃	850	$2201 \\ 2201 + \beta(ss)$
48	0.83	1.04	0.60	1.05	2:2.5:1.4:2.5	$Y_3Ga_5O_{12}$ SrTiO ₃	850	2201 $2201 + \beta(ss)$
52	0.95	1.08	1.34	0.78	2:2.3:2.8:1.6	$Y_3Ga_5O_{12}$	850	2201 + 2212
53	1.00	1.31	3.02	1.21	2:2.6:6.0:2.4	$Y_3Ga_5O_{12}$ SrTiO ₃	850	2212 2201
60	0.77	1.45	2.26	1.33	2:3.8:5.9:3.5	$Y_3Ga_5O_{12}$ SrTiO ₃	850	2212 + 2223 2201 + 2212
61	0.69	1.62	1.49	1.32	2:4.7:4.3:3.8	$Y_3Ga_5O_{12}$ SrTiO ₃	850	2212 + 2223 2201 + 2212 +
64	0.71	1.30	1.32	1.21	2:3.7:3.7:3.4	SrTiO ₃	850	2201 + 2212 + 2223
65	0.78	1.37	1.46	1.26	2:3.5:3.7:3.2	$Y_3Ga_5O_{12}$ SrTiO ₃	850	2201 + 2212 + 2223 2201 + 2212 + 2223
69	0.21	1.07	0.74	0.37	2:10.2:7.0:3.5	$Y_3Ga_5O_{12}$	850	2212

^a*Note:* β (ss) = β -solid solution of Bi₂O₃ and SrO



Fig. 1. X-ray diffraction pattern of Bi-2201 phase (sample No. 44).

typical size of $10-30 \,\mu\text{m}$ were observed on the surface in some cases (see Fig. 4). The composition of these droplets determined by EMA differs from those of the compact layers. Thus, we believe that these droplets are likely formed at the end of the deposition process under undefined conditions.



Fig. 2. X-ray diffraction pattern of Bi-2212 phase (sample No. 69).

• Under the above-mentioned deposition conditions pure Bi-2201 and Bi-2212 phases were formed on both the Y₃Ga₅O₁₂ and SrTiO₃ substrates. Bi-2212 was formed at 850°C in cases when the flow rates ratios of Sr, Ca and Cu to Bi were significantly higher than the ideal



Fig. 3. X-ray diffraction pattern of Bi-2201 + Bi-2212 + Bi-2223 mixture (sample No. 64).



Fig. 4. Electron scanning micrograph (1 : 1000) of surface morphology of the Bi-2201 layer (sample No. 45), bright droplets formed at the end of the deposition process differ from Bi-2201 composition.

stoichiometry Bi : Sr : Ca : Cu = 2 : 2 : 1 : 2. For Bi/Ca ≈ 2 only Bi-2201 was formed. The Bi-2223 phase was found only in a mixture with Bi-2201 and Bi-2212 phases.



Fig. 5. Temperature dependence of induced voltage (AC magnetic response) for the film No. 64.

- The chemical composition of the deposited layers for runs No. 45, 52, and 69 obtained by EMA can be correlated with the phase composition determined by XRD under the assumption that some substitution of Ca for Sr occurs.
- Annealing of the as-grown films at temperatures close to the synthesis temperature improves the superconducting $T_{\rm C}$ (see Fig. 5).

It is obvious that there are some differences between the calculated equilibrium composition of the system Bi-Sr-Ca-Cu-O-C-H and the composition of deposited layers. In order to explain them it must be first noted that the composition of the deposited layers is, in general, controlled by several simultaneously acting thermodynamic, transport and kinetic factors. So the discrepancies between the model and the experiment can be explained by nonnegligible contribitions of transport and kinetic factors in this case.

Another explanation can be found in the thermodynamics itself. Numerous papers demonstrated that it is difficult to obtain the Bi-2223 phase without the addition of Pb which promotes its formation [2]. However, the formation of Bi-2223 phase was observed in our study. It is likely associated with the low thermodynamic stability of this phase at temperatures of interest. The Gibbs energy of reaction (R1) calculated from our thermodynamic data is $\Delta G^{\circ}_{R1} = -7.3$ kJ at T = 1123 K (850°C). This value is within the inaccuracy range of the estimated data and so it is not possible to decide unambiguously whether the Bi-2223 phase is stable or not. A more detailed inspection of the X-ray diffraction spectra of samples containing Bi-2223 phase reveals very broad peaks indicating that this phase is formed in very small clusters, or, more likely, in segregated stacking falts within the Bi-2212 matrix. The occurrence of such defects in the Ca-rich Bi-2212 phase has been evidenced [26] and does not directly imply the stability of the Bi-2223 as a single phase.

In the case of Bi-2201, the discrepancies can be explained by a different stoichiometric formula for strictly stoichiometric Bi₂Sr₂CuO₆ considered in the calculations and real nonstoichiometric Bi-2201 phase $Bi_{2+x}Sr_{2-y}CuO_z$ with pseudotetragonal symmetry. Indeed, another phase with monoclinic symmetry has been reported for ideal composition [27], which was not identified in our experiments. A precise thermodynamic model of nonstoichiometric Bi2+xSr2-vCuOz taking into account Bi substitution for Sr and Cu substitution for Bi (site balanced model [28]) would be necessary for an appropriate description of this phase. The same conclusion holds for the Bi-2212 phase which also shows a deviation from ideal stoichiometry due to the substitution of Bi for Sr, Sr for Ca and vice versa, as well as the occurrence of Bi-2223 and Bi-2201 stacking faults [26].

5. Conclusions

The optimal deposition conditions for superconducting BiSrCaCuO films prepared by MOCVD were studied. Both the theoretical approach using thermodynamic analysis of the Bi-Sr-Ca-Cu-O-C-H-Ar system and the experimental deposition from metalorganic precursors in cold-wall RF heated reactor were employed. Several discrepancies were found between the theoretical and experimental results. These are likely due to the assumptions made in the thermodynamic model as well as complicated evaporation of the β -diketonate precursors of Cu, Ca and Sr. Our calculations predict the formation of the Bi-2212 phase for the same nominal ratio of metallic components in the input gas while in the experiment an excess of Sr, Ca and Cu over Bi is required. For ideal stoichiometry Bi:Sr:Ca:Cu = 2:2:1:2 only the low $T_{\rm C}$ phase Bi-2201 is formed. Moreover, the high $T_{\rm C}$ Bi-2223 phase was observed in some deposited layers. However, its occurrence was not predicted by the calculations. Several prepared films revealed the transition into a superconducting state. The transition temperature $T_{\rm C}$ can be improved by post-annealing followed by slow cooling. The highest $T_{\rm C}$ reached to date was 71 K.

Acknowledgements

This work was supported by the Ministry of Education of the Czech Republic through Grant No. VS 96070.

References

- K.H. Dahmen, T. Gerfin, Prog. Crystal Growth Charact. 27 (1993) 117.
- [2] M. Leskelä, H. Mölsä, L. Niinistö, Supercond. Sci. Technol. 6 (1993) 627.
- [3] N. Kubota, T. Sugimoto, Y. Shiohara, S. Tanaka, J. Mater. Res. 8 (1993) 978.
- [4] K. Endo, Appl. Phys. (NY) 6 (1996) 523.
- [5] C. Vahlas, T. Besmann, J. Am. Ceram. Soc. 75 (1992) 2679.
- [6] A.S. Jordan, J. Electron. Mater. 24 (1995) 1649.
- [7] C. Vahlas, F. Maury, L. Gueroudji, Chem. Vap. Deposition 4 (1998) 69.
- [8] A. Hårsta, J.O. Carlsson, J. Crystal Growth 114 (1991) 507.
- [9] P. Voňka, J. Leitner, CALPHAD 19 (1995) 25.
- [10] P. Voňka, J. Leitner, CALPHAD 19 (1995) 305.
- [11] J. Leitner, M. Nevřiva, D. Sedmidubský, J. Stejskal, in: K.E. Spear (Ed.), Proceedings of the Ninth International Conference on High Temperature Materials Chemistry, Vol. 97-39, The Electrochemical Society, Pennington, NJ, 1997, p. 164.
- [12] J. Leitner, D. Sedmidubský, M. Nevřiva in: J. Čermák (Ed.), Proceedings of the Seventh Conference on Diffusion and Thermodynamics of Materials, Inst. Phys. Mater. AS CR, Brno, 1998, p. 1 (in Czech).
- [13] D. Risold, B. Hallstedt, L.J. Gauckler, H.L. Lukas, S.G. Fries, J. Phase Equilib. 16 (1995) 223.
- [14] O. Knacke, O. Kubaschewski, K. Hesselmann, Thermochemical Properties of Inorganic Substances, 2nd edition, Springer, Berlin, 1991.
- [15] M.W. Chase Jr., C.A. Davies, J.R. Downey Jr., D.J. Frurip, R.A. McDonald, A.N. Syverud, JANAF Thermochemical

Tables, 3rd edition, J. Phys. Chem. Ref. Data 14 (Suppl. No. 1) (1985)1

- [16] E.H.P. Cordfunke, R.J.M. Konings, Thermochemical Data for Reactor Materials and Fission Products, Elsevier, Amsterdam, 1990.
- [17] V.P. Glushko (Ed.), Thermodynamic Properties of Individual Substances, Vol. III, Nauka, Moscow, 1981 (in Russian).
- [18] E.H.P. Cordfunke, R.R. van der Laan, J.C. van Miltenburg, J. Phys. Chem. Solids 55 (1994) 77.
- [19] J.R. Taylor, A.T. Dinsdale, CALPHAD 14 (1990) 71.
- [20] B. Hallstedt, D. Risold, L.J. Gauckler, J. Amer. Ceram. Soc. 80 (1997) 1085.
- [21] K.T. Jacob, K.P. Jayadevan, Mater. Trans., JIM 38 (1997) 427.

- [22] B. Hallstedt, D. Risold, L.J. Gauckler, J. Amer. Ceram. Soc. 79 (1996) 353.
- [23] D. Risold, B. Hallstedt, L.J. Gauckler, J. Amer. Ceram. Soc. 80 (1997) 527.
- [24] D. Risold, B. Hallstedt, L.J. Gauckler, J. Amer. Ceram. Soc. 78 (1995) 2655.
- [25] J. Stejskal, Chem. Listy 93 (1999) 36.
- [26] K. Knížek, E. Pollert, D. Sedmidubský, J. Hejtmánek, J. Prachařová, Physica C 216 (1993) 211.
- [27] J. Darriet, F. Weill, B. Darriet, X.F. Zhang, J. Etourneau, Solid State Commun. 86 (1993) 227.
- [28] R.M. Fleming, S.A. Sunshine, L.F. Schneemayer, R.B. VanDover, R.J. Cava, P.M. Marsch, J.V. Waszczak, S.H. Glarum, S.M. Zahurak, Physica C 173 (1991) 37.