Influence of pH during sol-gel synthesis on the phase purity, elemental composition and electrical properties of $YBa_2Cu_4O_8$ superconductor

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The sol-gel processing of ceramic materials for advanced applications involves several steps starting from precursor synthesis and ending up with multicomponent metal oxide. In this work the influence of pH value of the initial solution on the final $YBa_2Cu_4O_8$ product is studied. According to the X-ray diffraction (XRD) analysis data, the best $YBa_2Cu_4O_8$ samples have been prepared maintaining the pH of sol solution at 5.5–6.0. However, all the samples contained several impurity phases if no complexing agent during the sol-gel process was used in the system. The results obtained from the elemental analysis and electrical properties of the samples synthesized were found to be in good agreement with the speciation analysis of metals and the results from powder XRD analysis data.

Key words: sol-gel chemistry, precursors, YBCO superconductors

INTRODUCTION

Among numerous studies on high-T_C superconducting compounds, the Y–Ba–Cu–O system is the most exhaustively studied so far. The $YBa_2Cu_4O_8$ (Y-124) superconducting compound is a member of the homologous series of compounds of the general formula $Y_2Ba_4Cu_{6+n}O_{14+n}$ (n = 0, 1, 2). It exhibits a superconducting transition temperature (T_C), at around 79–80 K. The Y-124 phase is thermodynamically stable, isostructural, stoichiometric, and thus is an ideal system to study different substitution effects. Moreover, its oxygen content has excellent thermal stability in different atmospheres. All these features make the Y-124 phase very interesting from a theoretical point of view as a model system for testing the general trends of high-temperature superconductors and also in view of possible applications [1, 2].

A major problem encountered in the preparation of compound $YBa_2Cu_4O_8$ under ambient conditions is the difficulty in obtaining a monophasic material, since at higher temperatures the Y-124 phase decomposes into $YBa_2Cu_3O_7$ and CuO, while at lower temperatures the synthesis does not proceed to completion. Previously we described a relatively simple aqueous acetate-tartrate sol-gel synthesis method for the preparation of monophasic superconducting $YBa_2Cu_4O_8$ [3, 4]. However, the optimization of parameters (the concentration of initial salts, pH, temperature, the nature and concentration of the complexing agent, order of mixing, etc.) of above-mentioned sol-gel process has been determined mostly in an experimental way, *i.e.* according to the desired properties of the final ceramic material.

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ISSN 0235–7216. Chemija (Vilnius). 2002. T. 13, Nr. 1

Therefore, we found it interesting to investigate the nature of the specific chemical features that are involved in the aqueous Y–Ba–Cu–O acetate-tartrate system during the sol-gel process. Clearly, the development of reliable procedures to ensure a possible control of the sol-gel process, *i.e.* hydrolysis and condensation of molecular precursors, offers potential advantages for the controlled synthesis of the transition metal oxide networks [5–7]. On the other hand, the homogeneous distribution of metals in the oxide network might be responsible for the electrical, optical and other physical properties of multicomponent metal oxide compounds [8–10]. Thus, the results of the systematic investigation of sol-gel process in the Y–Ba–Cu–O system could be successfully used to explore new "soft chemistry" synthethic routes for different related compounds. In this work, we studied the synthesis of Y-124 phase from different Y–Ba–Cu–O acetate gels obtained varying the pH values of initial solution. The aim was the optimization of acetate sol-gel route for the preparation of Y-124 superconductor showing the necessity to use the chelating agent in the aqueous gel process.

EXPERIMENTAL

A series of acetate gel precursor samples for the preparation of the superconducting $YBa_2Cu_4O_8$ oxides was synthesized by an aqueous sol-gel processing route. Stoichiometric amounts of the analytical grade Y_2O_3, $Ba(CH_3COO)_2$ and $Cu(CH_3COO)_2 \cdot H_2O$ were used as starting materials. First, in the sol-gel process the Y_2O_3 (0.003125 mol) was dissolved in 100 ml of 0.2 M CH_3COOH. After stirring for 10 h at 55–60 °C a clear solution was obtained. Next, barium acetate $Ba(CH_3COO)_2$ (0.0125 mol) and copper acetate $Cu(CH_3COO)_2 \cdot H_2O$ (0.025 mol), both dissolved in 50 ml of distilled water, were added to the yttrium acetate solution with adequate intermediate stirring at the same temperature. To determine the influence of pH on the process, a solution of 20% CH_3COOH or NH_3 (1:1) was added to the precursor solution to adjust the pH from 3.5 to 7.5. Finally, after concentrating for 8 h at 60–65 °C in an open beaker, the sol solutions turned into blue viscous gels. The obtained Y–Ba–Cu–O gels were dried in air at 80–100 °C. The precursor powders were calcined for 10 h at 800 °C (heating rate: 20–150 °C ⇒ ⇒ 5 °C/min., 150–350 °C ⇒ 2 °C/min., 350–800 °C ⇒ ⇒ 10 °C/min) in flowing oxygen, reground in an agate mortar, and again heated for 10 h at 800 °C, again reground, pelletized and annealed for 10 h at 800 °C in a flowing oxygen atmosphere at ambient pressure.

The synthesized YBCO oxides were characterized by means of powder X-ray diffraction analysis performed with a Philips MPD 1880 diffractometer, using $CuK\alpha_1$ radiation. The cation content in the obtained ceramics was analyzed by energy-dispersive spectrometry (EDS) in a JEOL 820 scanning electron microscope (SEM), using L, K lines. For comparison, the amount of metals in the specimens was also determined, using different methods of physicochemical analysis: Cu and Ba by atomic absorption spectrometry (AAS) [11] with Hitachi 170–50 equipment, and Y by photometric analysis (PHA) [12] with a KFK-3 photometer (λ = 670 nm). For determination of Cu and Ba by AAS and Y by PHA, the standard solutions of copper in the range of

Table 1. **Equilibrium constants for system Ba(II), Cu(II), Y(III)-acetate**

Reaction	Equilibrium constant	Reference
$Ba^{2+} + CH_3COO^- \overset{\beta_1}{\underset{\leftarrow}{\rightarrow}} Ba(CH_3COO)^+$	$\log\beta_1 = 1.15$	[14]
$Cu^{2+} + CH_3COO^- \overset{\beta_1}{\underset{\leftarrow}{\rightarrow}} Cu(CH_3COO)^+$	$\log\beta_2 = 2.23$	[14]
$Cu^{2+} + 2CH_3COO^- \overset{\beta_2}{\underset{\leftarrow}{\rightarrow}} Cu(CH_3COO)_2$	$\log\beta_2 = 3.63$	[14]
$Y^{3+} + CH_3COO^- \overset{\beta_1}{\underset{\leftarrow}{\rightarrow}} Y(CH_3COO)^{2+}$	$\log\beta_1 = 1.53$	[14]
$Y^{3+} + 2CH_3COO^- \overset{\beta_2}{\underset{\leftarrow}{\rightarrow}} Y(CH_3COO)^{+}{}_{2}$	$\log\beta_2 = 2.66$	[14]
$Y^{3+} + 3CH_3COO^- \overset{\beta_3}{\underset{\leftarrow}{\rightarrow}} Y(CH_3COO)_3$	$\log\beta_3 = 3.4$	[14]
$Y^{3+} + OH^- \overset{\beta_1}{\underset{\leftarrow}{\rightarrow}} Y(OH)^{2+}$	$\log\beta_1 = 10.5$	[15]
$Y^{3+} + 2OH^- \overset{\beta_2}{\underset{\leftarrow}{\rightarrow}} Y(OH)^{+}{}_{2}$	$\log\beta_2 = 19.8$	[15]
$CH_3COOH \overset{K_a}{\underset{\leftarrow}{\rightarrow}} CH_3COO^- + H^+$	$\log K_a = -4.56$	[16]
$Cu^{2+} + 2OH^- \overset{K_{s0}}{\underset{\leftarrow}{\rightarrow}} Cu(OH)_2$	$\log K_{s0} = -18.2$	[17]
$Y^{3+} + 3OH^- \overset{K_{s0}}{\underset{\leftarrow}{\rightarrow}} Y(OH)_3$	$\log K_{s0} = -24.5$	[14]

0.5–4 μg/ml, barium in the range of 20–90 μg/ml, and yttrium in the range of 0.05–0.7 μg/ml were used, respectively. A standard four-probe technique was used for measuring the temperature dependence of the resistivity in range 20–300 K.

The distribution of Cu(II), Y(III) and Ba(II) among the complexes and the concentration of free (uncomplexed) metal ions were calculated by solving a system of non-linear equations in terms of the Newton iteration method [13]. The values of the equilibrium constants used were taken from [14–17] and are listed in Table 1.

RESULTS AND DISCUSSION

The phase purity of the obtained compounds has been estimated by X-ray diffraction analysis. In Figs. 1 and 2, the XRD patterns of $YBa_2Cu_4O_8$ oxides synthesized using different pH values in the sol-gel process are presented. To facilitate the interpretation of XRD patterns of the synthesized samples, we included a comparison of the XRD patterns of superconducting members of the homologous series of $Y_2Ba_4Cu_{6+n}O_{14+n}$: (*a*) n = 0; Y-123 phase, $YBa_2Cu_3O_7$; (*b*) n = 1; Y-247 phase, $Y_2Ba_4Cu_7O_{15}$; and (*c*) n = 2; Y-124 phase, $Y_2Ba_4Cu_4O_8$ (Fig. 3). The purest samples were obtained when the pH value of sols was maintained between 5.5 and 6.0 (see Fig. 1A). One can see that the characteristic features of the orthorhombic Y-124 phase, the characteristic (113) and (108) diffraction lines at 2θ ≅ 34.4 and 35.8°, and the separation of (200) (020) (0014) at 2θ ≅ 47° and the (017) (111) diffraction lines at 2θ ≅ 33° are evident. However, the formation of impurity phases was also identified (marked with asterisks). The diffraction lines at 2θ ≅ 29° and 31° could be attributed to the $BaCuO_2$ and two weak lines at 2θ ≅ 36.4° and 38.5° to CuO. The X-ray diffraction pattern of a sample synthesized at pH = = 6.5 (Fig. 1B) is very similar to the previous one, and the splitting of the (200) (020) (0014) and the (017) (111) diffraction lines is evident. This suggests that heat treatment of precursor gel resulted in two major crystalline phases: Y-124 and the tetragonal non-superconducting Y-123 ($YBa_2Cu_3O_6$) phase [18, 19]. Besides, the intensities of the alrea-

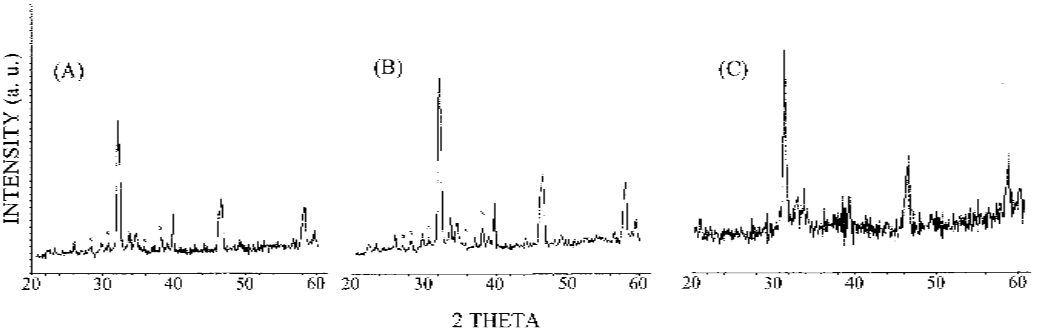

Fig. 1. XRD patterns of the $YBa_2Cu_4O_8$ oxides synthesized using different pH values in the sol-gel process: (A) 5.5; (B) 6.5; (C) 5.0. The impurity phases are marked with asterisks

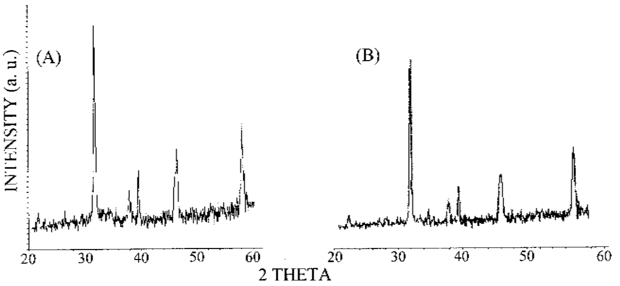

Fig. 2. XRD patterns of YBCO ceramic samples synthesized using different pH values in the sol-gel process: (A) 3.5; (B) 7.5

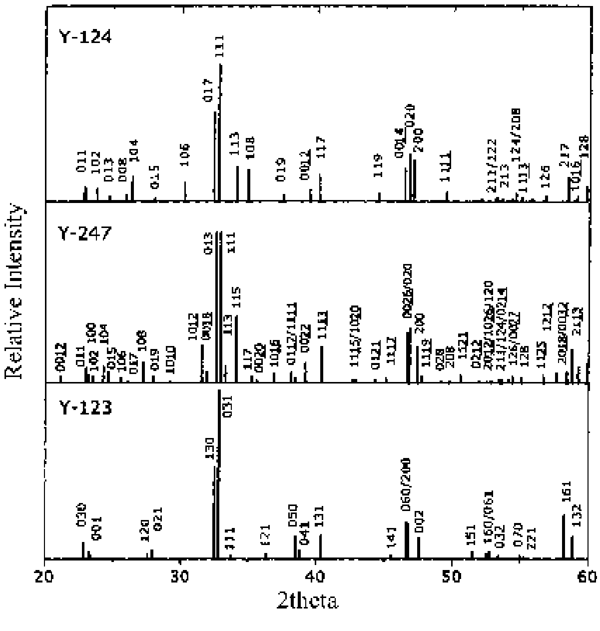

Fig. 3. Schematic presentation of the XRD patterns and Miller indices of Y-124, Y-247, and Y-123 phases from JCPDS © 1991 and 1996 reference data

dy mentioned impurity peaks are more pronounced. Morover, during annealing the minor amount of Y-211 impurity phase [20] has also formed. The X-ray diffraction patterns of samples prepared at lower pH values (pH 4.5–5.0) are also very similar. The representative X-ray diffraction pattern (pH 5.0) is shown in Fig. 1C. Its peculiarity is that the intensities of the peaks attributable to the CuO and $BaCuO_2$ impurity phases decrease. However, new diffraction lines at $2\theta \cong 27°$ and $39°$, possibly due to $BaCO_3$, and at $2\theta \cong 28°$ and $30°$ attributable to $Ba_2Cu_3O_5$ [21] are seen in the spectrum. The X-ray diffraction patterns of specimens prepared maintaining the lowest (3.5–4.0) and highest (7.0–7.5) pH values of the solutions during condensation process are very close. Two representative X-ray diffraction patterns are shown in Fig. 2. Evidently, the tetragonal non-superconducting Y-123 phase predominates in all of the cases, and only traces of the orthorhombic Y-124 phase could be detected. Besides, few additional peaks of unidentified phases are present in the spectra as well. Therefore, these results suggest that the pH of initial aqueous solutions in the sol-gel process should be adjusted with care. In addition, the single-phase sample of $YBa_2Cu_4O_8$ was prepared without using a complexing agent during gelation in a multicomponent system of metal acetates. Summarizing the powder X-ray diffraction analysis data, we can predict that during the high temperature calcination of precursor Y–Ba–Cu–O acetate gels prepared varying the pH of initial sol solutions, the following processes are possible:

$$\tfrac{1}{2}\ Y_2O_3 + 2\ BaO + 3\ CuO \Rightarrow YBa_2Cu_3O_{6.5} \quad (1)$$

$$4\ YBa_2Cu_3O_{6.5} + \tfrac{1}{2}\ O_2 \Rightarrow 2\ YBa_2Cu_4O_8 + Y_2BaCuO_5 + 3\ BaCuO_2 \quad (2)$$

$$2\ BaCuO_2 + CuO \Rightarrow Ba_2Cu_3O_5 \quad (3)$$

$$Y_2BaCuO_5 + 2\ Ba_2Cu_3O_5 + 2\ CuO + \tfrac{1}{2}\ O_2 \Rightarrow 2\ YBa_2Cu_4O_8 + BaCuO_2 \quad (4)$$

$$YBa_2Cu_4O_8 \Rightarrow YBa_2Cu_3O_7 + CuO \quad (5)$$

$$BaCO_3 \Rightarrow \text{unreacted.} \quad (6)$$

The main requirement for the sol-gel approach is to achieve a very high level of precursor homogeneity to give an excellent homogeneity in the final ceramic material. However, if the conditions of the sol-gel process are not optimized, precipitates during condensation reactions instead of a homogeneous gel network are formed [22]. Thus, heat-treatment of inhomogeneous gels produces inhomogeneous multiphase ceramic materials. To facilitate the interpretation of XRD analysis data, the stoichiometry of metals in the ceramic oxides was also determined. To check the metal contents in the annealed Y–Ba–Cu–O acetate gel powders, energy-dispersive spectrometry (EDS), atomic absorption spectrometry (AAS), and photometric analysis (PHA) were applied. The results are presented in Table 2. As is seen, most of the syntheses yielded inhomogeneous products, which is in good agreement with X-ray diffraction data. Again, the compositions nearest to the desirable metal ratio of Y : Ba : Cu = 1 : 2 : 4 were obtained when pH of initial solutions was 5.5 and 6.0. Commenting on the average metal molar ratio of Y : Ba : Cu presented in Table 1, it should be noted that in most cases it differs from that situated in the solution bulk, where the metal molar ratio of Y : Ba : Cu is precisely equal to 1.00 : 2.00 : 4.00. The deviation from the initial metal molar ratio presented in the solution could be accounted for the inhomogeneity of the ceramic obtained. AAS, PHA, and EDS results confirmed that various cations are inhomogeneously mixed and that there is plenty of segregation of the components.

Table 2. **Elemental analysis of ceramic materials prepared with pH control of the gels (n = 5)**

pH	Amount of metals (mol × 10^5)						Average molar ratio (Y : Ba : Cu)
	Y		Ba		Cu		
	EDS	PHA	EDS	AAS	EDS	AAS	
3.5	0,879	0,873	3.335	3.352	3.901	3.927	1.00 : 3.82 : 4.47
4.0	0.812	0.821	3.222	3.251	4.559	4.550	1.00 : 3.96 : 5.58
4.5	0.954	0.942	3.259	3.251	4.886	4.825	1.00 : 3.43 : 5.12
5.0	0.899	0.908	3.113	3.197	3.966	3.942	1.00 : 3.49 : 4.38
5.5	0.995	1.012	2.107	1.911	3.961	3.988	1.00 : 2.00 : 3.96
6.0	1.200	1.227	1.999	2.112	4.909	5.111	1.00 : 1.95 : 4.13
6.5	1.297	1.159	2.991	3.114	4.796	4.673	1.00 : 2.48 : 3.86
7.0	1.184	1.064	3.201	3.142	5.474	5.662	1.00 : 2.82 : 4.95
7.5	1.128	1.012	2.391	2.334	3.860	3.861	1.00 : 2.21 : 3.61

As already mentioned, the precursor gel powders prepared using different synthesis parameters were calcined for 30 h at 780 °C in flowing oxygen to obtain the Y-124 superconducting compound. All the specimens were found to be non-superconducting, except those synthesized from the precursor gel samples prepared when the pH of solutions was maintained 5.5 and 6.0. The resistivity measurements of a representative superconducting Y-124 sample are shown in Fig. 4. It is quite evident that the onset critical temperature of superconductivity ($T_{C(onset)}$) lies between 75–77 K. The observed $T_{C(onset)}$ value is almost consistent with the previously reported for the single-phase Y-124 superconductor (78 K [1]). However, $T_{C(zero)}$ values (48–56 K) were much lower in comparison with literature data (67–68 K). Thus, even the best samples show a rather broad transition to the superconducting state interval, which is about 20–30 K. It is interesting to note that the non-superconduting samples exhibited only a semiconducting behaviour (Fig. 5). Apparently, these ceramic powders contain different impurity phases which could be responsible for the different temperature dependence of their conductivity. This suggests that the pH value during gelation is the critical factor determining the nature and behaviour of the gel, which is of crucial importance for determining the good properties of a ceramic superconductor.

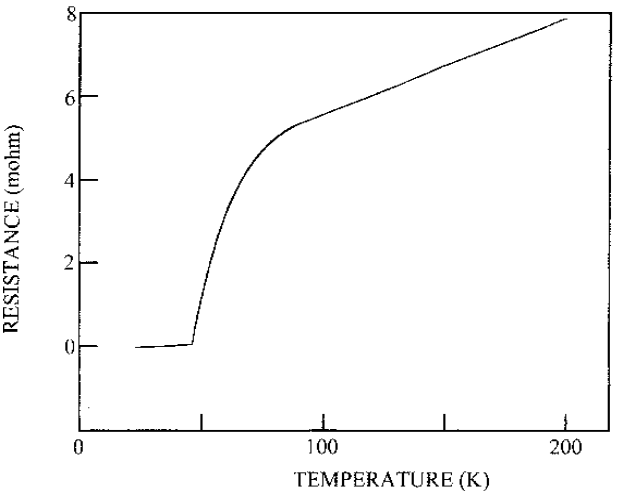

Fig. 4. Resistivity *vs.* temperature for the $YBa_2Cu_4O_8$ superconducting samples

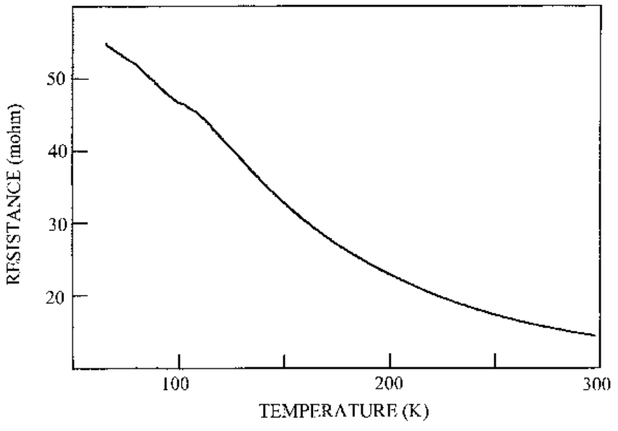

Fig. 5. Resistivity *vs.* temperature for the obtained non-superconducting oxide ceramics

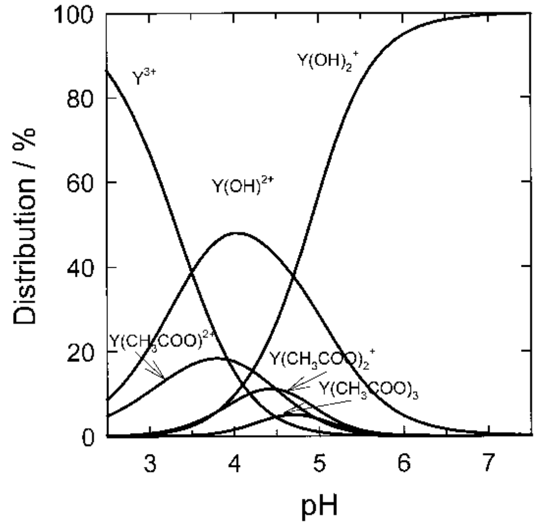

Fig. 6. Distribution of Y(III) among the complexes in solutions containing (M): $[CH_3COOH]_0$ – 0.20, $[Cu(II)]_0$ – 0.0625, $[Ba(II)]_0$ – 0.03125, $[Y(III)]_0$ – 0.015625

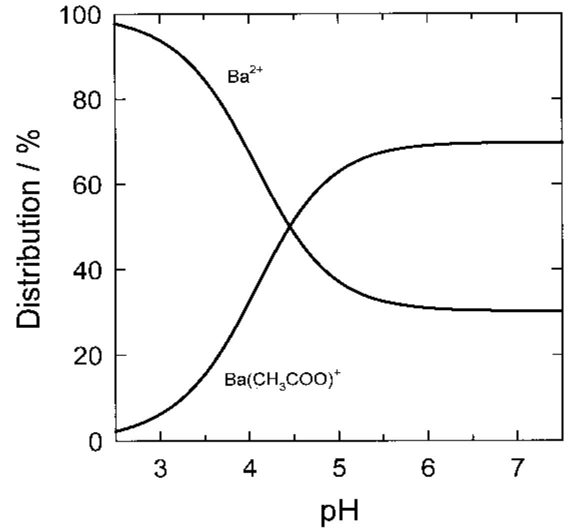

Fig. 7. Distribution of Ba(II) among the complexes in solutions containing (M): $[CH_3COOH]_0$ – 0.20, $[Cu(II)]_0$ – 0.0625, $[Ba(II)]_0$ – 0.03125, $[Y(III)]_0$ – 0.015625

The calculations showed that the distribution of Cu(II), Y(III) and Ba(II) among the complexes depends strongly on solution pH (Figs. 6–8). Equilibria in the solutions under investigation are rather

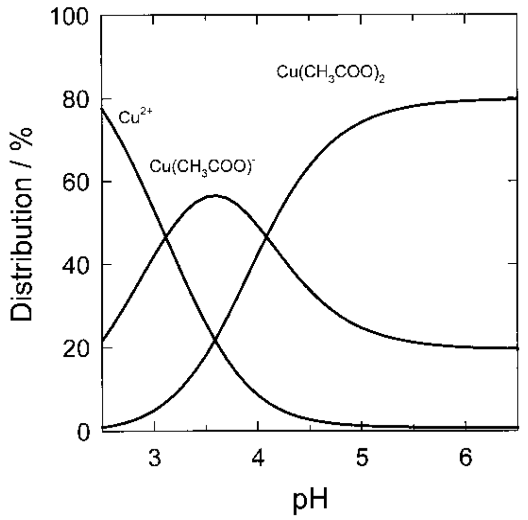

Fig. 8. Distribution of Cu(II) among the complexes in solutions containing (M): $[CH_3COOH]_0$ – 0.20, $[Cu(II)]_0$ – 0.0625, $[Ba(II)]_0$ – 0.03125, $[Y(III)]_0$ – 0.015625

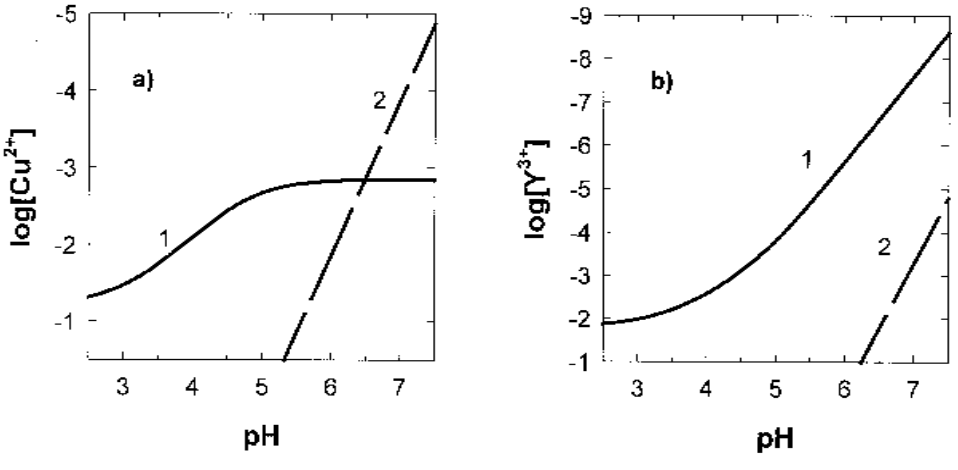

Fig. 9. Dependence of free (uncomplexed) Cu^{2+} (curve 1, a) and Y^{3+} (curve 1, b) ions on pH in solutions containing (M): $[CH_3COOH]_0$ – 0.20, $[Cu(II)]_0$ – 0.0625, $[Ba(II)]_0$ – 0.03125, $[Y(III)]_0$ – 0.015625. The dashed lines represent precipitation of $Cu(OH)_2$ (curve 2, a) and $Y(OH)_3$ (curve 2, b), respectively

complicated in the case of Y(III). No predominating species is observed in the pH range 3.5–5.0, while Y(III) aqua-ions predominate at lower pH and Y(III) dihydroxy-complex species at higher pH. Y(III)–acetate complexes in relatively small amounts are formed only at pH 2.5–6.0 (Fig. 6). Ba(II) ions exist in two forms in the solutions. Ba(II) aqua-ions prevail up to pH 4.5, and Ba(II)–monoacetate complex predominates with a further increase in pH (Fig. 7). The distribution of Cu(II) ions among the complexes (Fig. 8) shows that Cu(II) aqua-ions predominate only in strongly acid solutions, while Cu(II)–acetate complexes prevail at pH over 3.5 with predominating of Cu(II)–diacetate complex at pH over 4.5. It should be mentioned that no changes in complex distribution (as well as in concentration of free metal ions) are observed for Ba(II) and Cu(II) at pH over 6.3 due to the total deprotonization of acetic acid. Speaking about the possible influence of minor amounts of ammonia on the complex formation in the system under study, we can summarize that Ba(II) and Y(III) do not form complexes with ammonia, and the Cu(II)–monoammonia complex is formed in negligible quantities (less than 1%) at pH 6.0–6.5 and does not influence the general trend of complex formation.

The calculations of free metal ion concentration and its comparison with data on insoluble hydroxide formation presume formation of $Cu(OH)_2$ precipitate at pH over 6.5, while $Y(OH)_3$ precipitation is not expected in the pH range studied (Fig. 9). It should be noted that the data of the calculations are in good agreement with the experimental results. The solutions become turbid at pH over 6.5 due to precipitation of $Cu(OH)_2$, and the amount of the precipitates increases with the further increase in solution pH.

When comparing the results obtained with the equilibria in the solutions, we can find a clear correlation between the pH-dependent solution composition and the quality of the superconductor synthesized. The desirable samples were obtained at pH 5.5–6.0, when the predominant forms of Ba(II) and Cu(II) ions were Ba(II)–monoacetate and Cu(II)–diacetate species (see Figs. 7 and 8), while Y(III) exists in the form of hydroxy-complexes with dihydroxy-species predominating (Fig. 6). Poor quality samples were obtained at higher and lower pH, respectively. In the first case the results could be attributed to the precipitation of $Cu(OH)_2$ and formation of a disadvantageous heterogeneous system. At a lower pH limit (*e. g.*, 2.5–3.5) it is difficult to expect samples with a desirable molar ratio, because only metal aqua-ions predominate in the solutions.

CONCLUSIONS

The influence of pH value of the initial solution in the sol-gel process on the properties of the $YBa_2Cu_4O_8$

superconductor has been investigated. According to the X-ray diffraction analysis data, the best $YBa_2Cu_4O_8$ samples have been prepared maintaining the sol solution pH 5.5–6.0. The determined onset critical temperature of superconductivity ($T_{C(onset)}$) of these samples lies between 75–77 K. X-ray diffraction patterns of the specimens prepared maintaining the lowest (pH 3.5–4.0) and highest (pH 7.0–7.5) pH values of the solutions during condensation showed the formation of the tetragonal non-superconducting Y-123 phase along with unidentified impurity phases, and only traces of the orthorhombic Y-124 phase could be detected. These ceramic samples were found to be non-superconduting and exhibited only a semiconducting behaviour. The data of speciation analysis of metals are in good agreement with the experimental results.

Received 17 January 2002
Accepted 24 January 2002

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ZOLIO PH SINTEZĖS PROCESE ĮTAKA $YBA_2CU_4O_8$ SUPERLAIDININKO ELEMENTINEI IR FAZINEI SUDĖČIAI BEI ELEKTRINĖMS SAVYBĖMS

Santrauka

Ištirta tirpalų pH (nuo 3,5 iki 7,5) zolių-gelių sintezės procese įtaka $YBa_2Cu_4O_8$ (Y-124) superlaidininko elementinei ir fazinei sudėčiai bei elektrinėms savybėms. Iš Rentgeno spindulių difrakcinių tyrimų rezultatų nustatyta, kad nė vienu atveju nepavyko gauti vienfazio Y-124 junginio. Mažiausiai šalutinių fazių sintezės produktuose rastasz tais atvejais, kai tirpalų pH = 5,5 ir 6,0. Matuojant šiomis sąlygomis gautų Y-124 oksidų varžos priklausomybes nuo temperatūros nustatyta krizinė superlaidumo temperatūra T_C (pradžios), kuri kinta nuo 75 iki 77 K. Jeigu zolių tirpalų pH reikšmės buvo mažesnės arba didesnės, sintezės produktuose vyravo kitos priemaišinės kristalinės fazės. Nustatytas šių junginių varžos priklausomybės nuo temperatūros puslaidininkinis pobūdis. Įdomu pažymėti, kad metalų fizikinių ir cheminių formų pasiskirstymo tirpaluose skaičiavimo duomenys koreliuojasi su gautais eksperimentiniais rezultatais.