

# Evidence for the formation of superconducting phases in the Y–Ba–Ca–Cu–O system

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New high-temperature copper oxide superconductors in the Y–Ba–Ca–Cu–O system were synthesized using the sol-gel method. The superconducting properties of the synthesized mixed-metal cuprates were determined from magnetic susceptibility measurements. The samples with nominal compositions of  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-d}$  and  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-d}$  showed superconductivity at a  $T_C$  (onset) of approximately 82 K and 80 K, respectively. The materials were also characterized by X-ray powder diffraction, thermogravimetric analysis, scanning electron microscopy and energy-dispersive spectrometry.

**Key words:** superconducting materials, multinary compounds, cuprate superconductors

## INTRODUCTION

Ever since the first high-temperature copper oxide superconductor was discovered in the La–Ba–Cu–O system in 1986, a variety of high-temperature superconductors containing copper ions have been synthesized. There have been thousands of publications reporting the crystal structures of high-temperature cuprate superconductors, with the goal of clearly showing the structural requirements for high-temperature superconductivity in the cuprate phases. Most of the known cuprate superconductors belong structurally to a single family and are closely related to each other [1–3].

The search for the mechanisms of high-temperature superconductivity and novel superconducting materials are the most challenging tasks of condensed-matter physicists as well as material scientists [4–8]. Among numerous studies on high- $T_C$  superconducting compounds, however, the Y–Ba–Cu–O system is best studied so far [9–18]. The yttrium barium copper oxide  $\text{YBa}_2\text{Cu}_3\text{O}_7$  or  $\text{CuBa}_2\text{YCu}_2\text{O}_7$ , often called Y-123 or Cu-1212 superconducting compound, is the first member of the homologous series of compounds of the general formula  $\text{Y}_2\text{Ba}_4\text{Cu}_{6+n}\text{O}_{14+n}$  ( $n = 0, 1, 2$ ). The Cu-1212 phase exhibits a highest superconducting transition temperature ( $T_C$ ) inside the YBCO family (at around 90–92 K) and till now remains the most extensively studied high- $T_C$  superconductor [19–24].

Superconductivity at about 94 K has been recently discovered in  $\text{HgBa}_2\text{CuO}_{4+\delta}$  (Hg-1201) [2]. Hg-1201 has an unusually high  $T_C$  for a compound with a single  $\text{CuO}_2$  layer, and this phase is the first member of the Hg-based homologous series of layered Cu mixed oxides. The structure of the Hg-based superconductors  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$  ( $n = 1, 2, 3, \dots$ ) can be described as a sequence of layers: ... [(BaO) ( $\text{HgO}_8$ ) (BaO) ( $\text{CuO}_2$ ) – {(n–1) (Ca) ( $\text{CuO}_2$ )}] (BaO) ..., in which blocks (BaO) ( $\text{HgO}_8$ ) (BaO) having the rock-salt structure alternate with blocks (CuO) {(n–1) (Ca) ( $\text{CuO}_2$ )} having a perovskite-like structure. Thus, the Hg-1201 superconductor exhibits single octahedral copper layers interconnected through  $\text{HgO}_2$  sticks. The second member,  $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$  (Hg-1212), exhibits superconductivity at approximately 126 K and consists of double pyramidal copper layers interconnected by  $\text{HgO}_2$  sticks. A layer of Ca atoms is located between the  $\text{CuO}_2$  sheets in eightfold coordination with oxygen. The third member with the highest  $T_C \approx 133$  K,  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  (Hg-1223), is characterized by triple copper layers interconnected through  $\text{HgO}_2$  sticks. These three consecutive  $\text{CuO}_2$  sheets are separated by two Ca layers [2].

By analogy with the Hg-based cuprates, we have tried to introduce additional CaO layers into the structure of the  $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$  (Cu-1212 or Cu-12102) superconductor. The purpose of the present work was to prepare using the sol-gel synthesis method new superconducting phases: (a) having a single layer of CaO between two  $\text{CuO}_2$  sheets with the nominal composi-

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tion of  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9.8}$  (Cu-12113), and (b) having two CaO layers between triple CuO layers with the composition of  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11.8}$  (Cu-12124). The results of this study are presented below.

## EXPERIMENTAL

Superconducting  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9.8}$  and  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11.8}$  samples were prepared by the acetate–tartrate sol-gel method developed previously for the synthesis of the pure  $\text{YBa}_2\text{Cu}_3\text{O}_8$  superconductor [25]. As starting compounds, stoichiometric amounts of analytical grade  $\text{Y}_2\text{O}_3$ ,  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ,  $\text{Ba}(\text{CH}_3\text{COO})_2$  and  $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  were used. In the sol-gel process  $\text{Y}_2\text{O}_3$  was first dissolved in 0.2 M acetic acid solution by stirring at 55–60 °C. In the next step, mixtures of the appropriate amounts of  $\text{Ba}(\text{CH}_3\text{COO})_2$ ,  $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ , and  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ , all dissolved in small amounts of distilled water, were added with continuous stirring during several hours at the same temperature. An aqueous solution of tartaric acid was added to the reaction mixture to adjust the pH to 5.6, thus preventing crystallization of metal acetates during gelation [26]. The obtained solution was concentrated by slow evaporation (8 h) at 65 °C in an open beaker. When nearly 90% of the water had been evaporated under continuous stirring, a transparent blue gel was formed. After further drying in an oven at 80 °C, a fine-grained powder was obtained. The precursor powders were placed in an alumina crucible and calcined for 5 h at 800 °C in flowing oxygen, reground carefully in an agate mortar, and again heated for 5 h at the same temperature. After another grinding step, the intermediate precursor powders were palletized and annealed for another 10 h at 950 °C in a flowing oxygen atmosphere at ambient pressure. The heating and cooling rate was 5 °C min<sup>-1</sup>. At the end of the growth experiment the pellets were cooled in a furnace to 200 °C, and the crucible was raised outside the furnace. Finally, the obtained YBCCO ceramics were annealed for 10 h at 500 °C in oxygen to be converted into an orthorhombic superconducting form [27, 28].

The synthesized samples were characterized by X-ray powder analysis (STOE Powder Diffraction System) using  $\text{CuK}\alpha_1$  radiation. The  $T_c$  values of superconducting compounds were obtained from magnetic susceptibility measurements performed in gelatin capsules with a SQUID magnetometer (Quantum Design, MPMS) in the temperature region between 5 and 120 K at  $H = 20$  Oe. The TGA measurements were performed on a STA 490 analyzer (Netzsch) in an oxygen atmosphere at a heating rate of 5 °C/min. A JEOL JSM 6400 scanning electron microscope (SEM) was used to study the morphology, microstructure and the chemical composition of the ceramic samples. The cation content was analyzed by energy dispersive spectrometry (EDX) in a SEM using L, K lines.

## RESULTS AND DISCUSSION

The homogeneous Y–Ba–Ca–Cu–O acetate–tartrate precursor gel powders were calcined for 20 h at different temperatures in oxygen flow to obtain superconducting oxide ceramic compounds. X-ray diffraction data of the Cu-12113 sample are presented in Table 1. One can see that all single lines are indexed, and no unindexed lines could be observed. The most intensive lines are (110) – 100%, (013) – 73.5%, (123) – 26.1%, and (113) – 22.3%. 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  $\text{Y}_2\text{Ba}_4\text{Cu}_{6+n}\text{O}_{14+n}$ : (a)  $n = 0$ ; Y-123 phase,  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ; (b)  $n = 1$ ; Y-247 phase,  $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ ; and (c)  $n = 2$ ; Y-124 phase,  $\text{Y}_2\text{Ba}_4\text{Cu}_9\text{O}_{17}$  (Fig. 1). The X-ray diffraction data of Cu-12113 phase are close to the X-ray diffraction spectrum of Y-123 superconducting phase. However, the intensities, indexing, consequently the combinations of the diffraction lines are different. Moreover, the most intensive diffractions are slightly shifted in comparison with the diffraction peaks in the spectrum of Y-123 phase. Besides, some diffraction lines are present only in the spectra of the investigated sample. On the other hand, diffraction lines (111) (141) (002) (032) of Y-123 phase are absent in the X-ray diffraction pattern of Cu-12113 sample. Therefore, these results suggest that the original  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9.8}$  product was obtained during the high-temperature calcination of Y–Ba–Ca–Cu–O precursor gel, and only traces of Y-123 might be present as the impurity phase.

X-ray diffraction data of Cu-12124 sample are presented in Table 2. The most intensive lines are

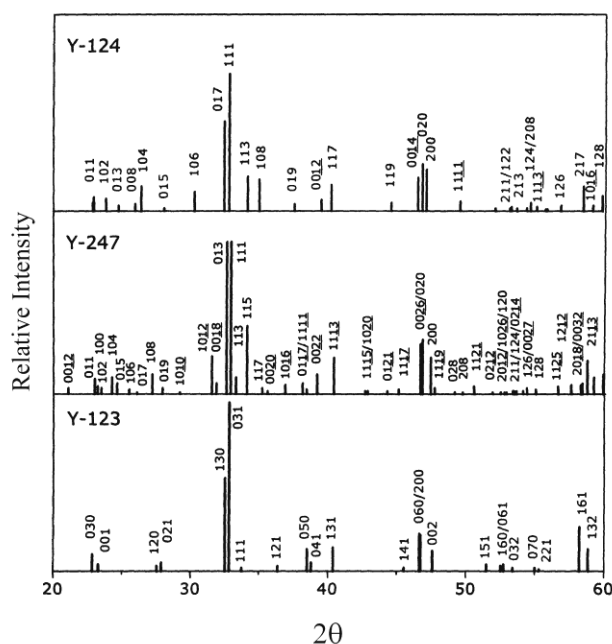


Fig. 1. Schematic presentation of XRD patterns and Miller indices of Y-124 Y-247, and Y-123 phases from JCPDS® 1991 and 1996 reference data

Table 1. X-ray powder diffraction data on  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9.8}$  sample. Number of indexed lines  $n = 21$ , unindexed lines  $n = 0$ 

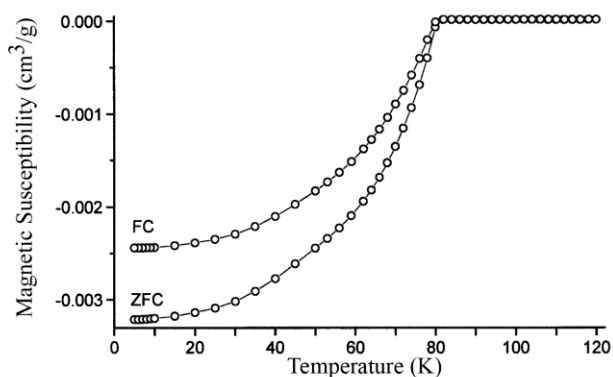
Miller indices			2 $\theta$ (observed), degrees	2 $\theta$ (calculated), degrees	d – spacing, Å	Intensity, %
h	k	l				
0	0	1	7.531	7.547	11.7045	13.3
0	0	2	15.136	15.127	5.8523	11.8
0	0	3	22.774	22.774	3.9015	11.7
1	0	0	23.054	23.131	3.8421	15.4
0	1	2	27.651	27.612	3.2280	16.8
1	0	2	27. 710	27.753	3.2118	16.5
0	1	3	32.594	32.563	2.7475	73.5
1	1	0	32.839	32.821	2.7265	100.0
1	1	2	36.331	36.320	2.4715	11.5
0	0	5	38.428	38.423	2.3409	16.4
0	1	4	38.527	38.541	2.3340	16.0
1	1	3	40.333	40.323	2.2349	22.3
0	0	6	46.508	46.516	1.9508	12.9
0	2	0	46.887	46.919	1.9349	19.9
1	1	5	51.405	51.405	1.7761	10.9
1	2	2	55.406	55.390	1.6574	9.7
1	1	6	58.097	58.095	1.5865	17.7
1	2	3	58.369	58.353	1.5801	26.1
0	1	7	60.203	60.245	1.5349	9.7
0	2	6	68.152	68.211	1.3738	10.6
2	2	0	68.836	68.810	1.3633	15.7

Table 2. X-ray powder diffraction data on  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11.8}$  sample. Indexed lines  $n = 26$ , unindexed lines  $n = 0$ 

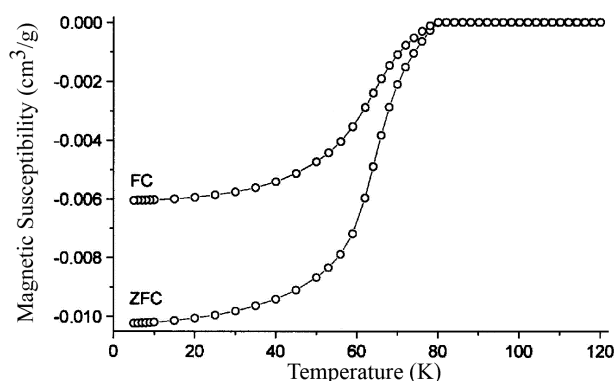
Miller indices			2 $\theta$ (observed), degrees	2 $\theta$ (calculated), degrees	d – spacing, Å	Intensity, %
h	k	l				
0	0	1	7.523	7.556	11.6901	15.3
0	0	2	15.155	15.146	5.8450	13.6
0	0	3	22.893	22.803	3.8967	15.1
1	0	0	23.244	23.242	3.8241	11.3
0	1	2	27.632	27.602	3.2291	10.5
1	0	2	27. 850	27.857	3.2001	11.5
0	1	3	32.575	32.566	2.7473	47.6
3	0	1	32.862	32.786	2.7293	100.0
1	1	1	33.858	33.789	2.6506	13.5
1	1	2	36.382	36.386	2.4672	9.4
0	0	5	38.498	38.473	2.3380	13.3
1	0	4	38.739	38.748	2.3220	8.1
1	1	3	40.389	40.393	2.2312	23.3
0	0	6	46.587	46.577	1.9483	12.4
0	2	0	46.833	46.867	1.9370	20.6
2	0	0	47.553	47.515	1.9120	15.6
1	1	5	51.484	51.488	1.7734	7.9
2	0	3	53.401	53.327	1.7165	5.2
0	0	7	54.955	54.936	1.6700	4.7
1	1	6	58.193	58.187	1.5842	19.2
2	1	3	58.807	58.791	1.5694	15.0
2	0	5	62.765	62.723	1.4801	6.2
1	1	7	65.531	65.527	1.4234	5.4
0	2	6	68.162	68.218	1.3736	6.9
1	0	8	68.740	68.710	1.3650	9.5
2	2	0	68.941	68.956	1.3607	13.0

(301) – 100%, (013) – 47.6%, (113) – 23.3% and (020) – 20.6%. The negligible difference in the intensities of the diffraction lines as compared to X-ray diffraction data of Cu-12113 sample is evident. However, X-ray diffraction patterns for both  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9.8}$  and  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11.8}$  compounds are very similar. Only a few additional peaks are present in the Cu-12124 sample. No diffraction peaks attributed to the possible common impurity phases such as  $\text{Y}_2\text{BaCuO}_5$ ,  $\text{BaCuO}_2$ ,  $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$ ,  $\text{BaCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{CuO}$ , and  $\text{CaO}$  could be detected from the X-ray diffraction data.

The lattice parameters of the synthesized samples were obtained from the diffraction spectra by fitting the peaks of identified reflections. The refined parameters of the orthorhombic lattice and cell volume were found to be  $a = 3.8421(14)$  Å,  $b = 3.8699(12)$  Å,  $c = 11.7045(20)$  Å,  $V = 174.03(7)$  Å<sup>3</sup> for the  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9.8}$  and  $a = 3.8241(11)$  Å,  $b = 3.8739(14)$  Å,  $c = 11.690(4)$  Å,  $V = 173.18(12)$  Å<sup>3</sup> for the  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11.8}$ . The orthorhombicity, here defined as  $b/a$ , evidently increases from 1.0072 to 1.0130 with increasing metal–oxygen layers in the structure of the synthesized oxides.



**Fig. 2.** Magnetic susceptibility vs. temperature for  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9.8}$  sample

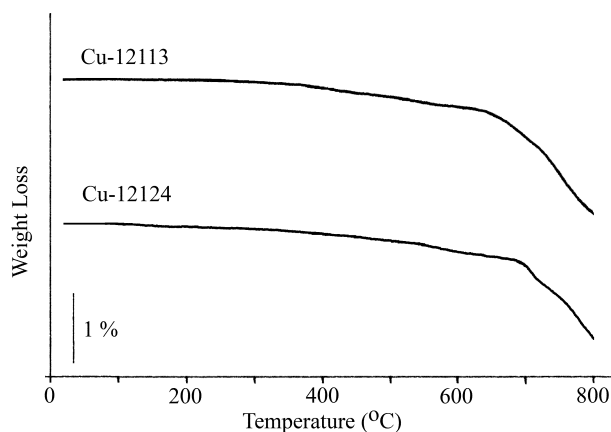


**Fig. 3.** Magnetic susceptibility vs. temperature for  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11.8}$  sample

The magnetic susceptibility *versus* temperature (FC = field cooled and ZFC = zero field cooled) measurements performed on as-prepared Cu-12113

and Cu-12124 samples are presented in Figs. 2 and 3, respectively. Both specimens were found to be superconducting having  $T_c$  (onset) = 82 K (for Cu-12113) and  $T_c$  (onset) = 80 K (for Cu-12124). It is interesting to note that the observed  $T_c$  values for Cu-12113 and Cu-12124 samples were quite different from those of the members of the homologous series of  $\text{Y}_2\text{Ba}_4\text{Cu}_{6+n}\text{O}_{14+n}$  [29]. Again, the  $T_c$  (onset) found to be about 80–82 K, for both of the samples synthesized allow to conclude that new phases have formed during the final heat treatment of the Y–Ba–Ca–Cu–O precursor gels.

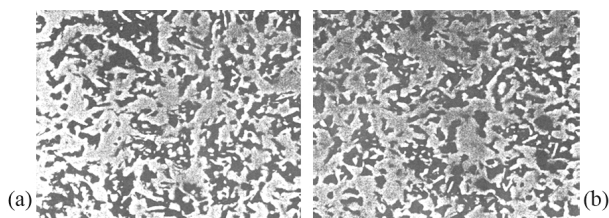
This hypothesis is also supported by the thermogravimetric analysis (TGA) of superconducting end products. In order to detect small amounts of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ,  $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$  and  $\text{Y}_2\text{Ba}_4\text{Cu}_4\text{O}_8$  impurities, the differences in the stability towards oxygen might be taken into account. For instance, oxygen in the Cu–O chains of the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  superconductor is not stable. Therefore, the Y-123 phase starts to lose the Cu–O chain oxygen around 300–400 °C [30]. When the Y-247 phase is heated in an oxidizing atmosphere, it shows a reversible weight loss between 570 °C and 850 °C due to a release of oxygen from the single Cu–O chains in the Y-123 blocks [30]. On the other hand, the Y-124 phase exhibits an excellent thermal stability up to 670–700 °C in an inert atmosphere, up to 830 °C in air and up to 860–890 °C in oxygen atmosphere [25, 31]. Figure 4 shows the TG curves of heating under oxygen atmosphere for the  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9.8}$  and  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11.8}$  samples. The mass of both Cu-12113 and Cu-12124 samples decreases negligibly and evenly starting from ~250 °C up to ~600–650 °C. From these temperatures a sharper weight loss was observed in both cases. The total weight losses in the temperature range from 20 to 800 °C of ~2.1% and ~1.7% were observed for Cu-12113 and Cu-12124 superconducting samples, respectively. Such an unusual thermal behaviour of synthesized products supports the results obtained from XRD



**Fig. 4.** Thermogravimetric curves in flowing oxygen atmosphere of  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9.8}$  and  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11.8}$  samples. The heating rate was 10 °C/min

and magnetic susceptibility measurements, indicating that the samples prepared are new multimetallic oxide phases.

The textural properties of the superconducting  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-\delta}$  and  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-\delta}$  samples were investigated by SEM, from which the grain size and typical morphologies were obtained. The SEM micrographs showed that a micrograin network is formed, keeping a glassy-like outline with no internal porosity. The formation of monodispersed plate-like crystallites with an average grain size of less than 2–3  $\mu\text{m}$  was observed from SEM micrographs. Figure 5 shows the SEM micrographs (back scattered electron (BSE) images) of the  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-\delta}$  and  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-\delta}$  pellets. Since the brightness of the specimens is homogeneous over the entire measuring area, the major part of the samples has a homogeneous structure and the distribution of its chemical elements is highly uniform.

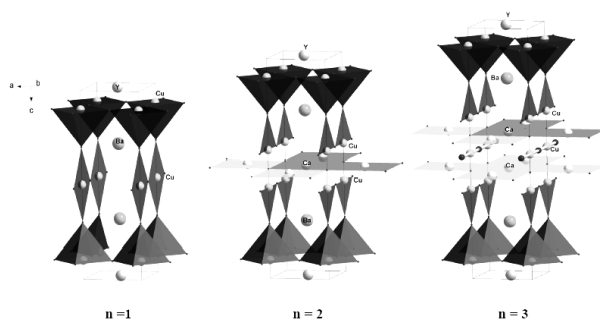


**Fig. 5.** Scanning electron micrographs of  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-\delta}$  (a) and  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-\delta}$  (b) superconductors in back-scattered electron mode. Magnification: 4000 $\times$

The elemental composition calculated from EDX analyses is in accordance with those of the  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-\delta}$  and  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-\delta}$  phases, and no metal-rich or Y-124, Y-123, or Y-247 phases were observed. However, some darker parts were also observed, their EDX elemental analysis proved it to be copper oxide. Since this was not detected by X-ray diffraction measurements, we can conclude that either the formation of amorphous CuO occurred [32] or the synthesized samples contained very small amounts of the impurity phase. Thus, SEM measurements of the heat-treated pellets of  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-\delta}$  and  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-\delta}$  samples are in accordance with the results from X-ray, magnetic susceptibility and TGA measurements.

The detailed characterization of the obtained cuprate superconductors led us to the conclusion that we synthesized a new Y–Ba–Ca–Cu–O superconducting system having the crystal structure related to  $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$  with additional calcium oxide layers between  $\text{CuO}_2$  sheets (analogously as in Hg-based superconductors). We have derived the general formula for this new homologous family of superconducting cuprates  $\text{CuBa}_2\text{YCa}_{n-1}\text{Cu}_{n+1}\text{O}_{5+2n-\delta}$  ( $n = 1, 2, 3, \dots$ ). The first members of this new series are: (i)  $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$ ; Cu-12102 ( $n = 1$ ); (ii)

$\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-\delta}$ ; Cu-12113 ( $n = 2$ ); (iii)  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-\delta}$ ; Cu-12124 ( $n = 3$ ). The possible structural models for the homologous series of  $\text{CuBa}_2\text{YCa}_{n-1}\text{Cu}_{n+1}\text{O}_{5+2n-\delta}$  are presented in Fig. 6.



**Fig. 6.** Structural models for homologous series of  $\text{CuBa}_2\text{YCa}_{n-1}\text{Cu}_{n+1}\text{O}_{2n+5+\delta}$  ( $\delta = 0$ )

## CONCLUSIONS

New superconducting  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-\delta}$  and  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-\delta}$  cuprates were prepared by the aqueous sol-gel method. The homogeneous Y–Ba–Ca–Cu–O precursor gel powders were calcined for 20 h at 950  $^\circ\text{C}$  in an oxygen flow with intermediate grindings. According to the powder X-ray diffraction analysis and thermogravimetric analysis, no evidence for the formation of related impurity phases, such as  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ,  $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ , and  $\text{Y}_2\text{Ba}_4\text{Cu}_4\text{O}_8$ , or other was observed. The magnetic susceptibility measurements revealed that  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-\delta}$  and  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-\delta}$  oxides to be superconducting samples having  $T_C$  (onset) = 82 K and  $T_C$  (onset) = 80 K, respectively. The SEM and EDX measurements of the heat-treated pellets of  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-\delta}$  and  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-\delta}$  samples were found to be in accordance with the results from X-ray, magnetic susceptibility and TGA measurements. The results obtained in this study allow to conclude that  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-\delta}$  and  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-\delta}$  compounds can be attributed to a new homologous family of superconducting cuprates, such as  $\text{CuBa}_2\text{YCa}_{n-1}\text{Cu}_{n+1}\text{O}_{5+2n-\delta}$  ( $n = 1, 2, 3, \dots$ ).

## ACKNOWLEDGEMENTS

The authors wish to thank Prof. H.-J. Meyer, Tübingen University, Germany for the use of equipment and helpful discussions.

Received 26 November 2004

Accepted 3 December 2004

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#### NAUJŲ SUPERLAIIDŲ FAZIŲ Y-BA-CA-CU-O SISTEMOJE SUSIDARYMO TYRIMAI

##### Santrauka

Zolių-gelių metodu vandeniniuose tirpaluose buvo susintetinti nauji superlaidūs  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-d}$  ir  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-d}$  mišrūs metalo kupratai. Šie keraminiai oksidai buvo gauti, kaitinant Y-Ba-Ca-Cu-O gelius 20 h  $950^\circ\text{C}$  temperatūroje deguonies atmosferoje. Pasirėmus rentgeno spindulių difrakcinės analizės rezultatais nustatyta, kad susidarę junginiai yra vienfaziai, t. y. jų difrakciniuose spektruose neaptiktos tikėtinos dalutinės  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ,  $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ ,  $\text{Y}_2\text{Ba}_4\text{Cu}_4\text{O}_8$  ar kitos fazės. Pagal magnetinio jautrio priklausomybės nuo temperatūros matavimo duomenis nustatyta, kad  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-d}$  junginiui krizinė pradžios superlaidumo temperatūra yra lygi 82 K, o  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-d}$  – 80 K. Padaryta išvada, kad šie kupratiniai superlaidininkai gali priklausyti naujai kupratinių superlaidininkų šeimai, kurios homologinių narių bendroji formulė yra  $\text{CuBa}_2\text{YCa}_{n-1}\text{Cu}_{n+1}\text{O}_{5+2n-d}$ .