

## Superconductivity in the Y-Ba-Ca-Cu-O system

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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 [1–3]. The yttrium barium copper oxide (YBCO)  $\text{YBa}_2\text{Cu}_3\text{O}_7$  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 general formula  $\text{Y}_2\text{Ba}_4\text{Cu}_{6+n}\text{O}_{14+n}$  ( $n = 0, 1, 2$ ). Cu-1212 phase exhibits a highest superconducting transition temperature ( $T_C$ ) inside YBCO family, at around 90–92 K, and till now remains the most extensively studied high- $T_C$  superconductor [4–8]. By the analogy to the Hg-based cuprates [9], we have tried to introduce additional CaO layers to the structure of  $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$  (Cu-1212 or Cu-12102) superconductor. The purpose of the present work was to prepare new superconducting phases using the sol–gel synthesis method: (a) having a single layer of CaO between two  $\text{CuO}_2$  sheets with the nominal composition of  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-\delta}$  (Cu-12113), and (b) having two CaO layers between triple CuO layers with the composition of  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-\delta}$  (Cu-12124). The results of this study are presented herein.

$\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-\delta}$  and  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-\delta}$  samples were prepared by an acetate-tartrate sol–gel method developed previously for the synthesis of pure  $\text{YBa}_2\text{Cu}_3\text{O}_7$  superconductor [10]. 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. After stirring the mixture for 10 hr in a beaker covered with a watch-glass a clear solution was obtained. 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 of them 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 [11]. The obtained solution was concentrated by slow evaporation (8 hr) 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 blue powder was obtained. The precursor powders were placed in alumina crucible and calcinated for 5 hr at 800 °C in flowing oxygen, re-ground carefully in an agate mortar, and again heated for 5 hr at the same temperature. After another grinding step, the intermediate precursor powders were palletized and annealed for another 10 hr at 950 °C in a flowing oxygen atmosphere at ambient pressure. The heating and cooling rate was 5 °C  $\text{min}^{-1}$ . At the end of the growth experiment the pellets were cooled in the furnace to 200 °C, and crucible was raised outside the furnace. Finally, the obtained yttrium barium calcium copper oxide (YBCCO) ceramics were annealed for 10 hr at 500 °C in oxygen to be converted into the orthorhombic superconducting form [12, 13].

The synthesized samples were characterized by X-ray powder analysis (STOE Powder Diffraction System) using  $\text{CuK}\alpha_1$  radiation.  $T_C$  values of superconducting compounds were obtained from magnetic susceptibility measurements performed in gelatine capsules with a SQUID magnetometer (Quantum Design, MPMS) in the temperature region between 5 and 120 K. Scanning electron microscope (SEM) JEOL JSM 6400 was used to study the morphology, microstructure, and chemical composition of the ceramic samples. The cation content was analyzed by energy dispersive spectrometry (EDX) in a SEM using L, K lines.

X-ray diffraction patterns of Cu–12113 and Cu–12124 samples are presented in Figs 1 and 2, respectively. The most intensive lines for Cu–12113 sample are (110)–100% observed at  $2\theta = 32.8^\circ$ , (013)–73.5%

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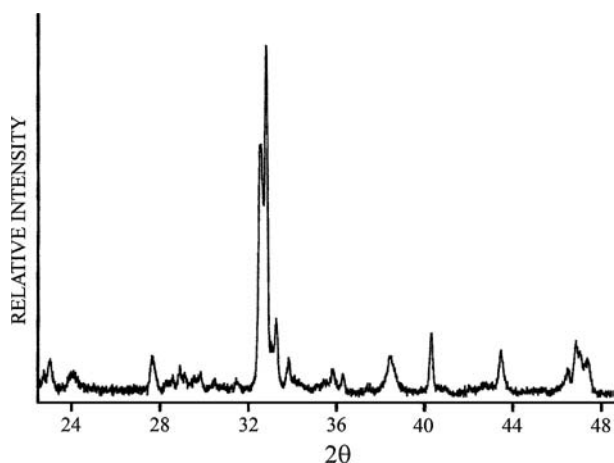


Figure 1 Powder XRD pattern of  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-\delta}$  superconductor synthesized by aqueous sol-gel technique.

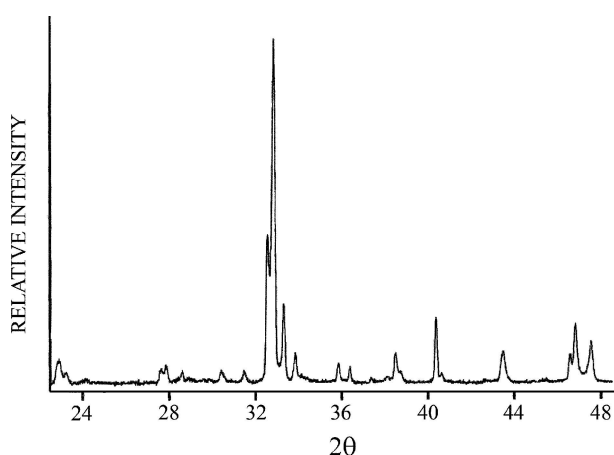


Figure 2 Powder XRD pattern of  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-\delta}$  superconductor synthesized by aqueous sol-gel technique.

at  $2\theta = 32.6^\circ$ , and (113)–22.3% at  $2\theta = 40.4^\circ$ . The most intensive lines for Cu-12124 are (301)–100% observed at  $2\theta = 32.8^\circ$ , (013)–47.6% at  $2\theta = 32.6^\circ$ , and (113)–23.3% at  $2\theta = 40.4^\circ$ . The X-ray diffraction patterns for both  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-\delta}$  and  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-\delta}$  compounds are very similar. Only few additional peaks are present in the Cu-12124 sample. No diffraction peaks attributable 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 patterns. Therefore, these results suggest that original  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-\delta}$  and  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-\delta}$  products were obtained during high temperature calcination of Y-Ba-Ca-Cu-O precursor gels.

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  $a = 3.8421(14) \text{ \AA}$ ,  $b = 3.8699(12) \text{ \AA}$ ,  $c = 11.7045(20) \text{ \AA}$ ,  $V = 174.03(7) \text{ \AA}^3$  for the  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-\delta}$  and  $a = 3.8241(11) \text{ \AA}$ ,  $b = 3.8739(14) \text{ \AA}$ ,  $c = 11.690(4) \text{ \AA}$ ,

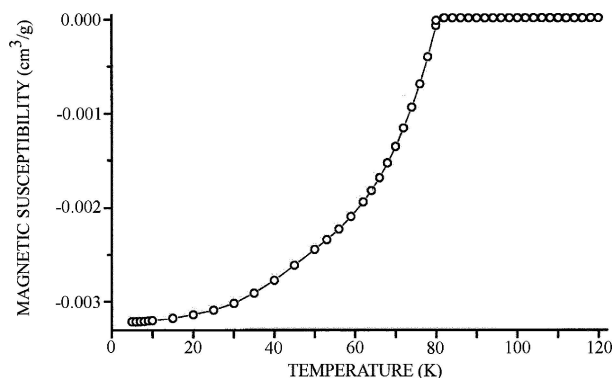


Figure 3 Zero-field cooled magnetic susceptibility versus temperature curve of the  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-\delta}$  sample.

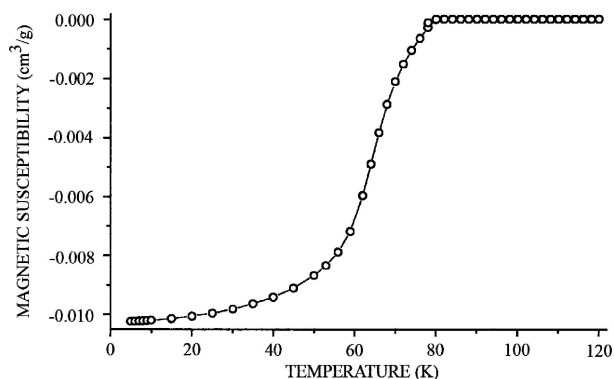


Figure 4 Zero-field cooled magnetic susceptibility versus temperature curve of the  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-\delta}$  sample.

$V = 173.18(12) \text{ \AA}^3$  for the  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-\delta}$ . The orthorhombicity, here defined as  $b/a$ , evidently increases from 1.0072 to 1.0130 with increasing metal-oxygen layers in the structure of synthesized oxides.

The magnetic susceptibility versus temperature measurements are presented in Figs 3 and 4. Both specimens found to be superconducting having  $T_C(\text{onset}) = 82 \text{ K}$  (for Cu-12113) and  $T_C(\text{onset}) = 80 \text{ K}$  (for Cu-12124). It is interesting to note that the observed  $T_C$  values for Cu-12113 and Cu-12124 samples are quite different from that of the members of the homologous series of  $\text{Y}_2\text{Ba}_4\text{Cu}_{6+n}\text{O}_{14+n}$  [14] leading us to conclude that new phases have formed during the final heat treatment of the Y-Ba-Ca-Cu-O precursor gels.

The difference between  $T_C$  values can also be related with different oxygen content in these compounds. It is known that the change in oxygen content causes a copper valence change and affects the  $T_C$  of the superconductors [15–17]. On the other hand, the critical temperature of superconductivity of related Hg-based  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$  superconducting compounds initially increases from 94 K (for the  $n = 1$  compound, Hg-1201) to a maximum of  $T_C \approx 135 \text{ K}$  (for the  $n = 3$  compound, Hg-1223). However, the  $n = 4$  and  $n = 5$  members (Hg-1234 and Hg-1256, respectively) were found to exhibit much lower  $T_C$  values, suggesting

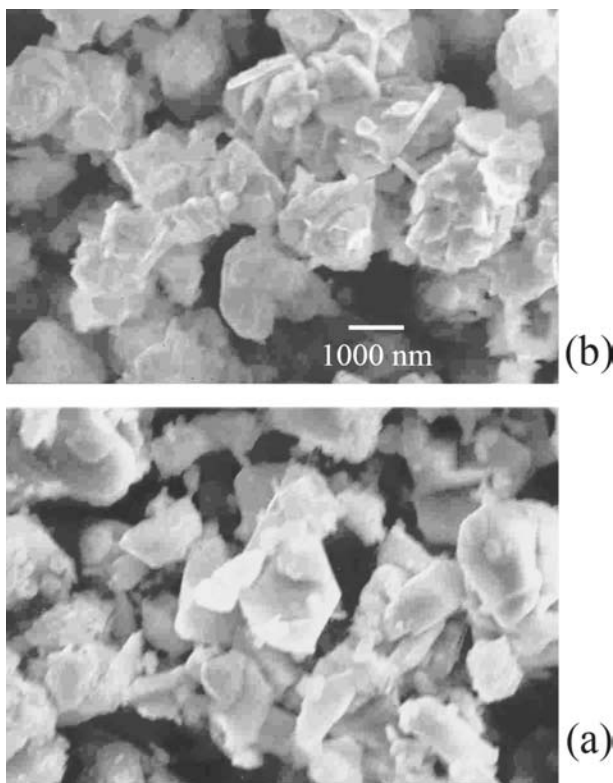


Figure 5 SEM micrographs of  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-\delta}$  (a) and  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-\delta}$  (b) superconductors.

that with further increasing Cu-oxide layers in the structure of these materials the  $T_C$  decreases [18, 19].

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. Fig. 5 shows SEM micrographs of  $\text{CuBa}_2\text{YCaCu}_3\text{O}_{9-\delta}$  and  $\text{CuBa}_2\text{YCa}_2\text{Cu}_4\text{O}_{11-\delta}$  pellets. As seen, there are no any significant morphological differences between two investigated samples. It is clear that the specimens have grain boundaries composed of plate-shaped grains. These plate-like grains show various orientations and are tended to grow in slightly different directions forming a micrograin network. The cuprate particles prepared by sol-gel technique being small in size (less than  $2-3 \mu\text{m}$ ), a tendency towards agglomeration is observed. The elemental composition calculated from EDX analyses was 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 determined. Thus, SEM measurements 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 here in accordance with the results from X-ray and magnetic susceptibility measurements.

The detailed characterization of the obtained cuprate superconductors lead us to a conclusion that a new Y-Ba-Ca-Cu-O superconducting system having crystal structure related to  $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$  with additional calcium oxide layers between  $\text{CuO}_2$  sheets has been synthesized.

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