

# Characterization of strontium-substituted Y-124 superconducting compounds

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Superconducting  $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$  samples ( $x = 0.05; 0.10; 0.15; 0.20$ ) were synthesized by an aqueous sol-gel method using Y-Ba(Sr)-Cu-O acetate-tartrate gel powders as starting materials. The thermal behaviour, phase purity, microstructural and morphological features of the synthesized samples were investigated by TGA/DTA, XRD, SEM, and elemental analysis methods. The oxygen stoichiometry in the strontium-substituted  $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$  superconducting samples was determined by a titrimetric analysis. It was determined that all the synthesized compounds showed oxygen nonstoichiometry. The amount of oxygen in the samples increased with the increase in the concentration of strontium. Moreover, it was demonstrated that  $T_C$  of  $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$  specimens increased almost linearly with an increasing oxygen content in the superconducting samples.

**Key words:**  $YBa_2Cu_4O_8$ , Y-124, sol-gel preparation, superconductors, strontium substitution effects

## INTRODUCTION

The search for high-temperature superconductivity and novel superconducting mechanisms is still one of the most challenging tasks of condensed-matter physicists as well as material scientists [1–5]. The studies on various substitutions in oxide superconducting systems have proven to be of great importance since changes in critical transition temperature are usually observed [6].

As a result, such doping basically can vary the hole concentration in a controlled manner influencing the superconducting properties of the materials obtained. Doping of different ions at the copper sites in the YBCO superconductor serves as a useful diagnostic probe to investigate the role of different copper sites for the occurrence of superconductivity in these superconductors. It is well recognized that the  $YBa_2Cu_4O_8$  (Y-124) phase is thermodynamically stable, isostructural, stoichiometric, oxygen content is thermally stable and thus is an ideal system to study different substitution effects [7–10].

Recently, monophasic strontium-substituted superconducting  $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$  samples have been synthesized by the aqueous sol-gel method [11–13]. The authors demonstrated that the critical temperature of superconductivity was enhanced from 78 K (for a non-substituted Y-124 sample) to 88 K (for the 20% strontium-substituted

sample  $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ ). An increase in the transition temperature cannot be explained directly by an increase in the hole concentration in  $CuO_2$  sheets, since an isovalent substitution occurs (replacement of  $Ba^{2+}$  by  $Sr^{2+}$ ). The existence of other superconducting phases such as Y-123 or Y-247 is not considered to be a reasonable explanation for the enhanced superconductivity properties since the characterization of the synthesized specimens using different techniques confirms that single-phase samples of  $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$  have been prepared.

It was also suggested that very small amounts of strontium enter the copper sites in the Y-124 structure [13]. Therefore, the authors using point-defect chemistry and quasi-chemical equations have explained the possible mechanisms of an increased charge carrier concentration in the  $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$  samples. However, it was not considered that the ionic radii of strontium and copper were different ( $Sr^{2+} \rightarrow 1.26 \text{ \AA}$ , and  $Cu^{2+} \rightarrow 0.57 \text{ \AA}$ ). Thus, it is difficult to believe that strontium ions enter the copper sites considering it in the crystallographic aspect.

It is well known that the  $T_C$  of superconducting cuprates slightly depends on the oxygen stoichiometry [14]. Moreover, despite the fact that the superconducting  $YBa_2Cu_4O_8$  is thermodynamically stable, isostructural and stoichiometric, a small variation of the oxygen content can be also detected [15]. In the work described herein, the  $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$  samples were synthesized by the

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same sol-gel chemistry approach and characterized using different techniques. Moreover, we tried to elucidate the reasons responsible for the increasing critical temperature of the superconductivity in Y-124 using the results of oxygen determination in the strontium-substituted Y-124 samples.

## EXPERIMENTAL

$Y(Ba_{1-x}Sr_x)_2Cu_4O_8$  samples with  $x = 0.05, 0.01, 0.15$  and  $0.20$  were prepared by an acetate-tartrate sol-gel method. As starting compounds, stoichiometric amounts of  $Y_2O_3$ ,  $Ba(CH_3COO)_2$ ,  $Sr(CH_3COO)_2$  and  $Cu(CH_3COO)_2 \cdot H_2O$ , all of them of analytical grade, were used. In the sol-gel process,  $Y_2O_3$  was firstly dissolved in 0.2 M of acetic acid at 55–60 °C. Next,  $Ba(CH_3COO)_2$ ,  $Sr(CH_3COO)_2$  and  $Cu(CH_3COO)_2 \cdot H_2O$ , all of them dissolved in a small amount of distilled water, were added during several hours at the same temperature with intermediate stirring. The obtained solutions were concentrated during about 8 hours at 60–65 °C in an open beaker. Under a continuous stirring, transparent blue gels formed. After further drying in an oven at 100 °C, fine grained blue powders were obtained. The precursor gel powders were calcined for 10 h at 780 °C in flowing oxygen, ground in an agate mortar, and again heated for 20 h at 780 °C, reground again, pelletized and annealed for 20 h at 780 °C in a flowing oxygen atmosphere under ambient pressure.

The oxygen content of  $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$  samples ( $x = 0.05, 0.01, 0.15$  and  $0.20$ ) was determined by the iodometric titration method [15]. The determination was performed by two iodometric titrations (A and B).

### Titration A

$Y(Ba_{1-x}Sr_x)_2Cu_4O_8$  sample was dissolved in 10 ml 1 M HCl. The titration beaker was put on a hot plate until boiling for a few minutes to ensure the whole  $Cu^{3+}$  is reduced. After cooling to room temperature, nitrogen gas was admitted to the beaker. Then 1.5 g of KI dissolved in a small amount of distilled water was added into the beaker. Nitrogen gas was then allowed to flow gently over the solution until the titration was completed. The solution was titrated with  $Na_2S_2O_3$ .

### Titration B

10 ml of HCl was mixed with 1.5 g of KI and nitrogen gas flowed over the solution all the time. Then  $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$  sample was added into the beaker and stirred thoroughly until all of the solid dissolved (about 1–2 minutes). 10 ml of distilled water was added and titrated with  $Na_2S_2O_3$ .

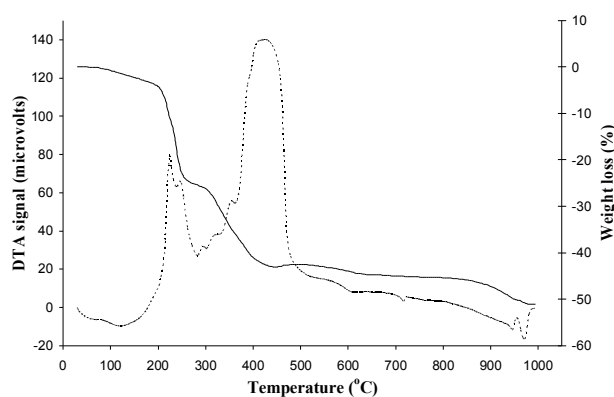
The synthesized samples were characterized by X-ray powder analysis performed with a Siemens D-500 diffractometer, using  $CuK\alpha_1$  radiation. TGA/DTA measurements were obtained in flowing air atmosphere using a Setaram TG-DSC12 analyzer. A scanning electron microscope (SEM) JEOL 820 was used to study the

morphology of the samples. FAAS determination of barium and strontium was performed using an atomic absorption spectrometer Hitachi 170-50.

## RESULTS AND DISCUSSION

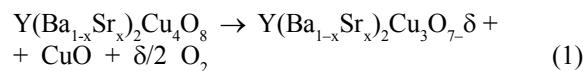
### Characterization of the gel precursors

Firstly, the obtained gel powders were characterized by the TGA/DTA method. The TGA/DTA curves for a Y-Ba(Sr)-O acetate-tartrate gel are shown in Figure 1. The TG curve shows three main weight losses in the temperature ranges: 20–200 °C (~6–7%), 200–250 °C (~20–22%) and 250–450 °C (~20%). The weight loss below 200 °C is due to the evaporation of water, solvent molecules or absorbed water. This feature is clearly confirmed by the endothermic effect in the DTA curve (~80–140 °C).



**Fig. 1.** TGA (solid line) and DTA (dotted line) curves of Y-Ba(Sr)-Cu-O acetate-tartrate gel with 20% Sr substitution

The main weight loss was observed between 200 and 450 °C (~40–42%). This decomposition step can be attributed to the pyrolysis of organic compounds and the degradation of intermediate species formed during the gelation process. This weight loss is accompanied by the endothermic peaks in the DTA curve (~220–250 °C and ~420–450 °C). In the TGA curve, a small weight loss (~3–4%) could be detected at around 880 °C. The endothermic effects at the same temperature are also seen in the DTA curve. These thermal changes can be related to the decomposition of Y-124 phase [16]:



All the precursor gels were characterized by the X-ray powder diffraction analysis. The XRD patterns of the Y-Ba(Sr)-Cu-O acetate-tartrate gels were identical regardless of the Sr substitutional level. The XRD pattern of the Y-Ba(Sr)-Cu-O gel having 15% of Sr is shown in Figure 2. As one can see, the XRD pattern of the obtained Y-Ba(Sr)-Cu-O gel shows broad peaks due to the amorphous character of the powders. We can see only the peaks around  $2\theta \approx 16.5$  and  $\approx 42.5$ , which have arisen from the used sample holder. No peaks due

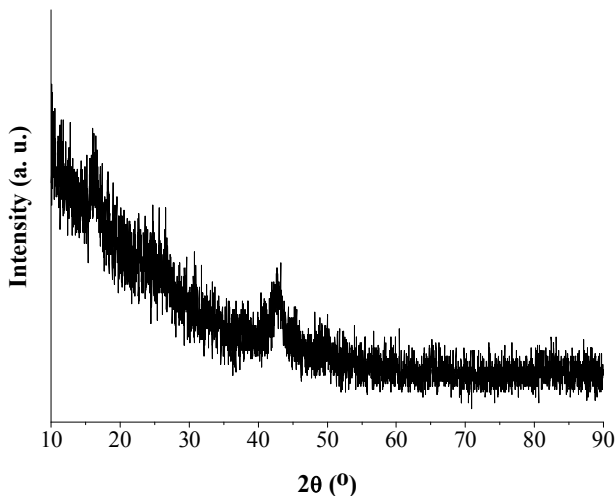


Fig. 2. X-ray diffraction pattern of Y-Ba(Sr)-Cu-O acetate-tartrate gel with 15% Sr substitution

to insignificant crystallization of metal acetates, tartrates, or crystallization of any undesired or contaminating phase could be identified. Such observation shows the individuality and high level of homogeneity of the synthesized Y-Ba(Sr)-Cu-O precursor gels.

#### Characterization of the end products

The Y-Ba(Sr)-Cu-O precursor gels were calcined at 780 °C. The amount of strontium and barium in the  $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$  samples was determined by flame atomic absorption spectroscopy (FAAS). The results of the determination are summarized in Table 1. From the results presented in Table 1, it is seen that the determined total amount of strontium and barium by FAAS method corresponds to the nominal ratio of these metals in Y-124.

The  $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$  oxides were characterized by X-ray powder diffraction analysis. Again, the XRD patterns of the Sr-substituted Y-124 samples were identical regardless of the Sr substitutional level. In Figure 3, the XRD pattern of  $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$  sample with a higher substitution level of Sr (20%) is shown. As one can see from Figure 3, all single lines are indexed showing the formation of the orthorhombic Y-124 phase. The XRD pattern also shows a high degree of crystallinity of the synthesized  $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$  oxide. The most intensive lines are (017), (111) around  $2\theta \approx 33^\circ$  and (0014), (020) and (200) around  $2\theta \approx 47^\circ$ . From the results of XRD we can conclude that the peaks of the Y-124 phase dominate in the whole investigated range of Sr substitution ( $x = 0.05-0.20$ ). Thus, the Sr-doping (up to

$x = 0.20$ ) in the crystalline structure of  $YBa_2Cu_4O_8$  does not have any influence on the phase composition of the synthesized samples.

The end products were characterized by scanning electron microscopy (SEM). The scanning electron micrographs showed that a micrograin network is formed, keeping a glassy-like outline with no internal porosity. Apparently, the limiting growth of the crystallites and high degree of crystallinity of  $Y(Ba_{0.80}Sr_{0.20})_2Cu_4O_8$  samples was obtained.

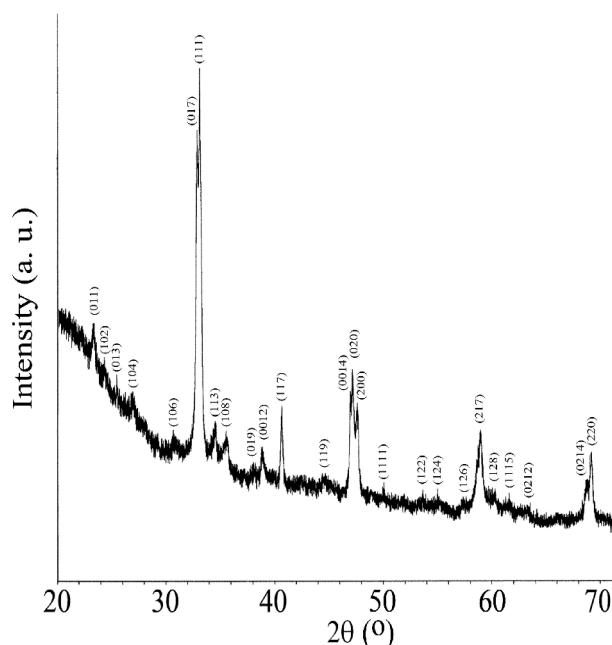


Fig. 3. Powder X-ray diffraction pattern of  $Y(Ba_{0.80}Sr_{0.20})_2Cu_4O_8$  sample.

#### Oxygen nonstoichiometry in the superconducting $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$

The results of iodometric titrations are summarized in Table 2. The results presented in Table 2 show that strontium-substituted Y-124 phases are oxygen nonstoichiometric. Such oxygen nonstoichiometry can be related with the difference in the ionic radii of  $Sr^{2+}$  and  $Ba^{2+}$  (1.18 Å and 1.35 Å, respectively). Thus, the general formula for different specimens of  $Y(Ba_{1-x}Sr_x)_2Cu_4O_{8-\delta}$  could be adjusted to  $(Y(Ba_{0.95}Sr_{0.05})_2Cu_4O_{7.82}, Y(Ba_{0.90}Sr_{0.10})_2Cu_4O_{7.85}, Y(Ba_{0.85}Sr_{0.15})_2Cu_4O_{7.87}$  and  $Y(Ba_{0.80}Sr_{0.20})_2Cu_4O_{7.89})$ .

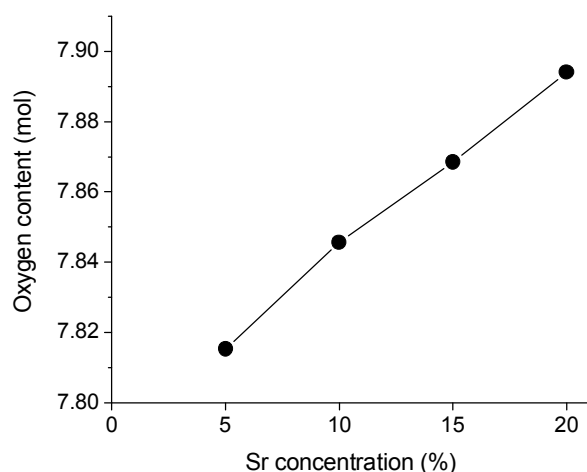
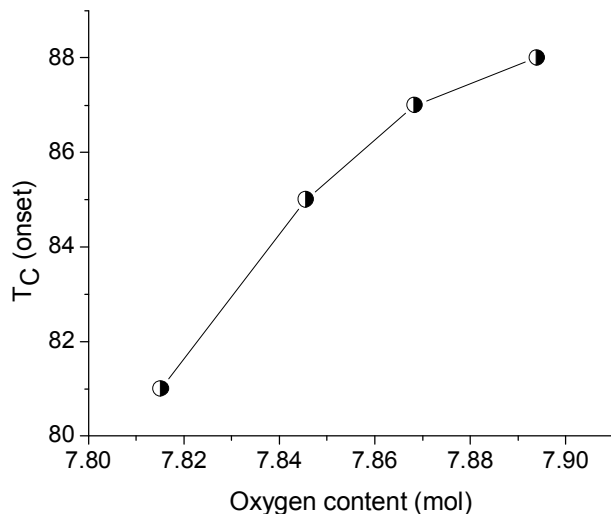
Interestingly, the oxygen content in the Y-124 phase increases with the increasing Sr concentration (see Fig. 4). Although the oxygen nonstoichiometry in Sr-substituted Y-124 samples is evident, the exact reasons for such cor-

Table 1. FAAS determination of strontium and barium in the  $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$  samples ( $n = 5$ )

Synthesized samples	Ba amount ( $10^{-5}$ ) mol	Sr amount ( $10^{-5}$ ) mol	Ba:Sr molar ratio
$Y(Ba_{0.95}Sr_{0.05})_2Cu_4O_8$	3.318(4)	0.175(3)	1.89 : 0.10
$Y(Ba_{0.90}Sr_{0.10})_2Cu_4O_8$	3.151(3)	0.351(2)	1.80 : 0.20
$Y(Ba_{0.85}Sr_{0.15})_2Cu_4O_8$	2.974(5)	0.519(3)	1.72 : 0.30
$Y(Ba_{0.80}Sr_{0.20})_2Cu_4O_8$	2.802(4)	0.695(3)	1.61 : 0.40

Table 2. Determination of the oxygen amount in the  $Y(Ba_{1-x}Sr_x)_2Cu_4O_{8-\delta}$  samples ( $n = 4$ )

Synthesized sample	O <sub>2</sub> content in Y-124 phase (mol)
$Y(Ba_{0.95}Sr_{0.05})_2Cu_4O_8$	7.815(2)
$Y(Ba_{0.90}Sr_{0.10})_2Cu_4O_8$	7.846(3)
$Y(Ba_{0.85}Sr_{0.15})_2Cu_4O_8$	7.868(3)
$Y(Ba_{0.80}Sr_{0.20})_2Cu_4O_8$	7.894(2)

Fig. 4. Correlation between the oxygen content and strontium concentration in  $Y(Ba_{1-x}Sr_x)_2Cu_4O_{8-\delta}$  samplesFigure 5.  $T_C$  dependence on the oxygen content in  $Y(Ba_{1-x}Sr_x)_2Cu_4O_{8-\delta}$  samples

relation is not completely clear. As it can be seen from Figure 4, the oxygen content increases almost linearly with the increasing Sr concentration. Thus, we can clearly state that the possible reason of the enhanced critical temperature of superconductivity in Sr-substituted Y-124 is the increasing oxygen content. In Figure 5, the critical temperature dependence on the oxygen content in  $Y(Ba_{1-x}Sr_x)_2Cu_4O_{8-\delta}$  is shown ( $T_C$  data from [13]). From Figure 5 one can see that  $T_C$  increases also almost li-

nearly with the increasing oxygen content in Sr-substituted Y-124 samples. Thus, we can conclude that the deviation from oxygen stoichiometry in  $Y(Ba_{1-x}Sr_x)_2Cu_4O_{8-\delta}$  superconducting oxides influences significantly the critical temperature of the superconductivity.

## CONCLUSIONS

Strontium-substituted  $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$  ( $x = 0.05, 0.01, 0.15$  and  $0.20$ ) samples were synthesized by the aqueous sol-gel method. The synthesized gels were found to be amorphous, highly homogeneous and individual compounds. The XRD measurements showed that all the single lines in the XRD patterns for all samples could be indexed and attributed to the orthorhombic Y-124 phase. The surface morphology investigation showed that a micrograin network is formed, keeping a glassy-like outline with no internal porosity, limiting the growth of the crystallites and a high degree of crystallinity of  $Y(Ba_{0.80}Sr_{0.20})_2Cu_4O_8$ . It was determined that all the synthesized compounds show oxygen nonstoichiometry. The oxygen content in the  $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$  samples increases with the increasing concentration of strontium. Moreover, it was demonstrated that the  $T_C$  of  $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$  specimens increases almost linearly with the increasing oxygen content in the superconducting samples.

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#### **STRONCIU PAKEISTO Y-124 SUPERLAIDININKO APIBŪDINIMAS**

##### **S a n t r a u k a**

Keturi  $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$  pavyzdžiai, kuriuose  $x = 0,05, 0,01, 0,15$  ir  $0,2$ , buvo susintetinti acetatinio-tartratinio zolių-gelių metodu. Deguonies kiekis  $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$  superlaidininkuose nustatytas klasikiniu jodometrinio titravimo metodu. Aptikta, kad stronciu pakeista Y-124 fazė yra nestechiometriška deguonies atžvilgiu. Nustatyta, kad deguonies kiekis  $Y(Ba_{1-x}Sr_x)_2Cu_4O_{8-\delta}$  superlaidininke ne tik didėja, didinant jame Sr kiekį, bet ir didėja tiesiškai. Parodyta, kad stronciu pakeistame Y-124 superlaidininke krizinė superlaidumo temperatūra ( $T_c$ ) didėja taip pat beveik tiesiškai didėjant deguonies kiekiui. Šie rezultatai leido padaryti išvadą, kad krizinės superlaidumo temperatūros padidėjimas  $Y(Ba_{1-x}Sr_x)_2Cu_4O_{8-\delta}$  superlaidininke, lyginant su nepakeistu  $YBa_2Cu_4O_8$  kupratu, yra susijęs su deguonies stochiometrijos pokyčiais.