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THE JOINT INFLUENCE OF CATION AND OXYGEN NONSTOICHIOMETRY ON SUPERCONDUCTING PROPERTIES IN 123 CUPRATE

As shown earlier, there is a "slow" constituent (γ) into oxygen nonstoichiometry in superconducting 123-cuprates doped with rear-earth elements. The aim of this paper is to study possible effect of changing "slow" oxygen content on electrophysical properties of HTSC cuprates. Magnetization of Sm-doped samples $YBa_{1.90}Sm_{0.10}Cu_3O_x$ was measured in a vibrating sample magnetometer in scanning magnetic field and temperature. Two series of samples $YBa_{1.90}Sm_{0.10}Cu_3O_{6+\delta+\gamma}$ were prepared for measurements from the same batch of material: with maxim (γ_{max} = 0.10) and minimum (γ_{min} = 0.00) values of "slow" oxygen content and corresponding to formulas $YBa_{1.90}Sm_{0.10}Cu_3O_{7.07}$ and $YBa_{1.90}Sm_{0.10}Cu_3O_{6.97}$ respectfully. Both types of samples were obtained from the same batch of sintered material. Samples (I) were brought to equilibrium at 720°C (lower than T_{b1}) to maximize the "slow" oxygen content: γ_{max} = 0.10. Then they were cooled to 400°C and kept at this temperature for 1 h to maximize "quick" oxygen content. The final total oxygen content in the samples of this series was established at x (I) = 7.07 ($YBa_{1.90}Sm_{0.10}Cu_3O_{7.07}$).

Samples (II) were brought to equilibrium at 900°C (above T_{b2}) to minimize the "slow" oxygen content: γ_{min} = 0.00 and then they were rapidly (in less then 10 min) cooled to and kept at 400°C for 1 h. The final total oxygen content in the samples of this series was equal to x (II) = 6.97 ($YBa_{1.90}Sm_{0.10}Cu_3O_{6.97}$).

The study of magnetic hysteresis in these samples shows that additional oxidation with respect to "slow" component produces HTSC with higher both the critical temperature T_c and intragrain critical current density J_{cg} in ceramic specimens. The maximum value of $J_{cg} \approx 3 \cdot 10^6$ A/cm^2 in untextured ceramic specimens was observed.

Key words: *high-temperature superconductor, cuprate, nonstoichiometry, magnetic hysteresis*

Introduction

A characteristic feature of high-temperature superconducting (HTSC) cuprates is a strong dependence of their structural and electrophysical properties on oxygen nonstoichiometry. Cuprates exhibit large oxygen nonstoichiometry: depending on temperature and oxygen partial pressure in the ambient, oxygen index *x* in barium-yttrium cuprate $YBa_2Cu_3O_x$ (YBCO) changes in the interval $6.2 < x < 7.0$ at equilibrum and in metastable state – from 6.0 to 7.0 [1,2]. Oxygen in YBCO exists in two forms: strongly and weakly bound. The strongly bound oxygen is in the state of oxidation -2 (usual for oxides) and its amount is constant: 6.0 mole O per formula unit. The weakly bound oxygen is evolved when cuprate is dissolved in acids and its oxidation number exceeds -2 (which is met, e.g., in peroxides). This form of oxygen is completely responsible for oxygen nonstoichiometry and its amount δ is a variable part of general oxygen content: $x = 6 + \delta$ [1, 2].

Earlier we found that in barium-yttrium cuprate $YBa_{2-y}RE_yCu_3O_x$ doped with a rear-earth (RE) element a new, additional constituent (γ) of oxygen nonstoichiometry is realized so that $x = 6 + \delta + \gamma$ [3,4]. Contrary to usually observed nonstoichiometric oxygen (δ), this additional part of nonstoichiometry shows a very slow kinetics of relaxation and also gives the possibility of oxygen content higher than 7 mole per formula unit: $x > 7{,}0$. According to these data, we need to distinguish two unlike components of weakly bound oxygen in nonstoichiometric cuprates: usual «quick» δ and additional «slow» γ. Slow oxygen appears in cuprates doped with heterovalent substitutes such as RE at Ba sites.

In air ambient, the highest content of «slow» oxygen may be obtained after keeping a sample to equilibrium below T_{b1} = 740ºC and this extra oxygen content equals to RE amount: $\gamma_{max} = y$. This implies the following scheme of Ba substitution for RE: $[Sm_{Ba}^{\bullet}] = [O_b']$. Above T_{b2} = 840ºC, "slow" oxygen is completely lost from the sample, $\gamma_{min} = 0$ [3,4].

The aim of this paper is to study possible effect of changing «slow» oxygen content on electrophysical properties of HTSC cuprates. Magnetization of Sm-doped samples $YBa_{1.90}Sm_{0.10}Cu_3O_x$ was measured in a vibrating sample magnetometer in scanning magnetic field and temperature.

Preparation of nonstoichiometric samples

Cuprate samples doped with Sm according to the formula $YBa_{2-y}Sm_yCu_3O_x$ (y = 0 – 0,10 with the step 0,02) were studied. Although the batch formula suggests itroduction of Sm instead Ba, ionic radii considerations (r(Y) = 1.02 Å, r(Sm) = 1.079 Å, r(Ba) = 1.42 Å), show that a change in stoichiometric ratio of large (as compared to Cu) cations at Y and Ba sites is expected: (Y+Sm)/Ba = (1+y)/(2–y).

The samples were synthesized through a standard ceramic procedure. As starting reagents Y_2O_3 («ITO-LUM»), CuO («pure for analysis»), $BaCO_3$ («highly pure 9-3»), and Sm_2O_3 («highly pure») were used. We focused on attaining homogeneous single-phased state of synthesized samples. Weighed portions of starting reagents were ground and mixed in an agate mortar under layer of ethanol. Mixed and ground powders were pressed into pellets and fired in air at 880–930°C for 30–40 hours. To improve the links between the grains of reacting substances, intermediate grindings of reaction mixtures were performed after each 6-8 hours during solid-state synthsis. The pattern of X-ray diffraction in Fig. 1 (a DRON-3 diffractometer, Cu K_α radiation) confirms completion of synthesis, single-phase state and good crystallinity of powder sample after firing at 920°C for 40 h.

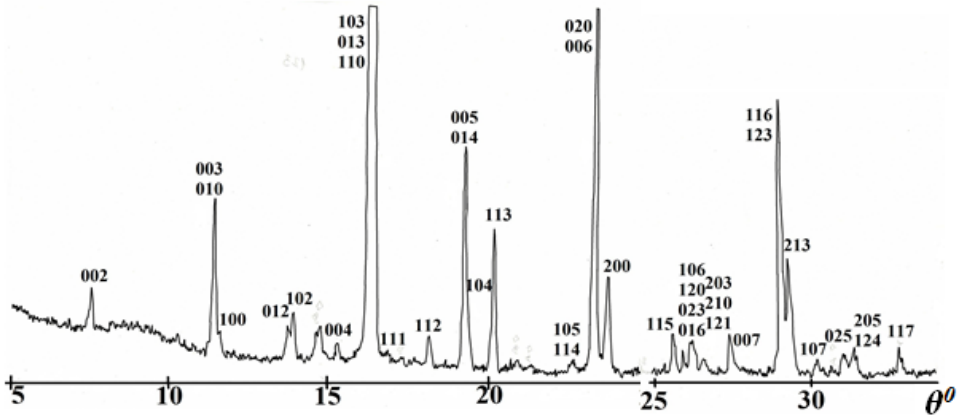

Fig. 1. X-ray powder diffraction pattern from single-phased $YBa_{1.90}Sm_{0.10}Cu_3O_x$ after synthesis at 920ºC for 40 h.

Finally, the samples of synthesized powders were formed into plates with dimensions 15 × 5 × 1 mm and sintered at 930-940ºC for 2–3 hours with the following slow cooling (<100ºC/h) to room temperature.

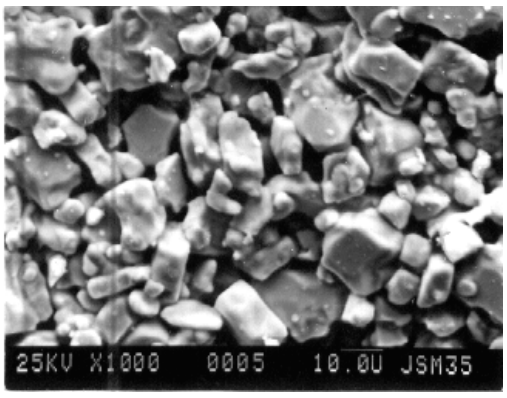

Fig. 2. SEM microphotograph of sintered sample $YBa_{1.90}Sm_{0.10}Cu_3O_x$ White segment = 10 μm.

The SEM microphotograph (JSM-35C, JEOL) taken from sintered sample (Fig.2) shows well formed crystalline grains, often platelike, with quite clear surfaces. They are distributed in sizes from 5 to 20 μm.

A series of electron probe local analyses taken from different grains of the sample (Fig.3) shows the presence of only one phase – 123 cuprate. Assessment of

the joint data of electron microscopy, X-ray diffraction and local electron probe analyses comes to unambigious conclusion that the sample presents a single-phased homogeneous 123 cuprate without any foreign phase inclusions.

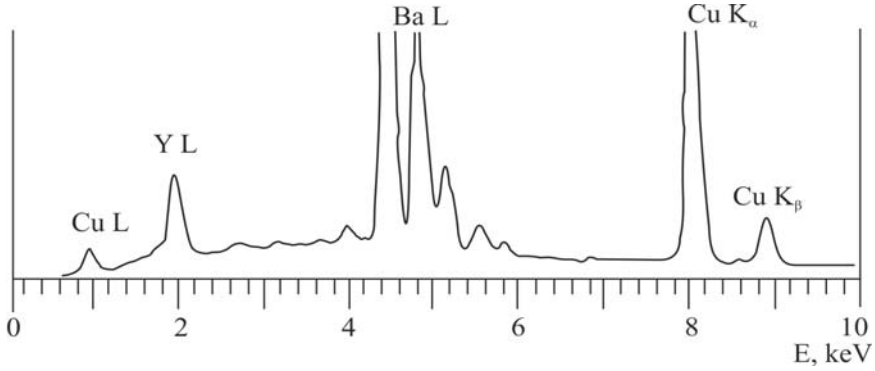

Fig. 3. A typical energy-dispersive spectrum of electron probe local analysis of sintered sample $YBa_{1.90}Sm_{0.10}Cu_3O_x$

Two series of samples $YBa_{1.90}Sm_{0.10}Cu_3O_{6+\delta+\gamma}$ were prepared for measurements: with maxim (I) and minimum (II) values of «slow» oxygen content: γ(I) = 0.10 and γ(II) = 0.00 respectfully. Both types of samples were obtained from the same batch of sintered material. Samples (I) were brought to equilibrium at 720°C (lower than T_{b1}) to maximize the "slow" oxygen content: γ_{max} = 0.10. Then they were cooled to 400°C and kept at this temperature for 1 h to maximize «quick» oxygen content. The final total oxygen content in the samples of this series was established at x (I) = 7.07 ($YBa_{1.90}Sm_{0.10}Cu_3O_{7.07}$).

Samples (II) were brought to equilibrium at 900°C (above T_{b2}) to minimize the «slow» oxygen content: γ_{min} = 0.00 and then they were rapidly (in less then 10 min) cooled to and kept at 400°C for 1 h. The final total oxygen content in the samples of this series was equal to x(II) = 6.97 ($YBa_{1.90}Sm_{0.10}Cu_3O_{6.97}$).

Results of magnetic measurements

Magnetic moments of samples were measured by a Foner's vibrating sample magnetometer (VSM). The measurements were conducted in scanning magnetic field (reversal field H_{max} = 8 kOe) and temperature (reversal point above T_c) modes.

In Fig. 4 temperature dependences of magnetization M of the samples I and II in heating-cooling cycles are compared.

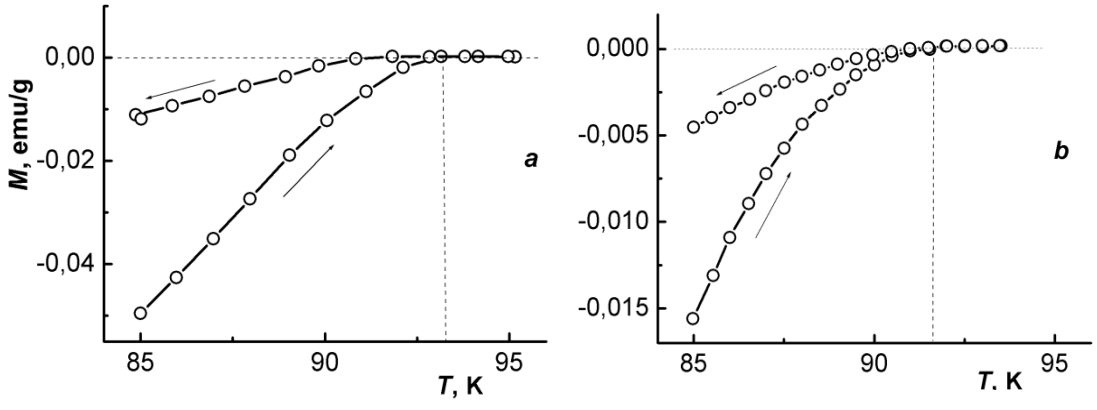

Fig. 4. Hysteresis of magnetization at thermocycling samples (I) – (a) and (II) – (b)

These measurements were performed in a low external field ($H \approx 2$ Oe) and with the reversal temperature well above the critical temperature T_c. A typical time period taken for measurements in a heating-cooling cycle starting and ending at about 5 K was half an hour.

Observed hysteresis is typical for type-II superconductors. Two branches of the hysteresis curve meet at the point that corresponds to the critical temperature T_c. At T_c a negative diamagnetic moment of a superconducting sample disappears. In Fig. 4 these points are indicated with vertical dashed lines.

As obtained from the data in Fig. 4, the critical temperature of sample I ($YBa_{1.90}Sm_{0.10}Cu_3O_{7.07}$) is T_c(I) = 93.4 K as compared to T_c(II) = 91.7 K for sample II ($YBa_{1.90}Sm_{0.10}Cu_3O_{6.97}$). Thus, maximizing «slow» oxygen content ($\gamma_{max} = 0.10$) may somewhat increase T_c.

Figure 5 demonstrates magnetic hysteresis loops taken from sample I ($YBa_{1.90}Sm_{0.10}Cu_3O_{7.07}$) at different temperatures, in this case at 5 and 75 K.

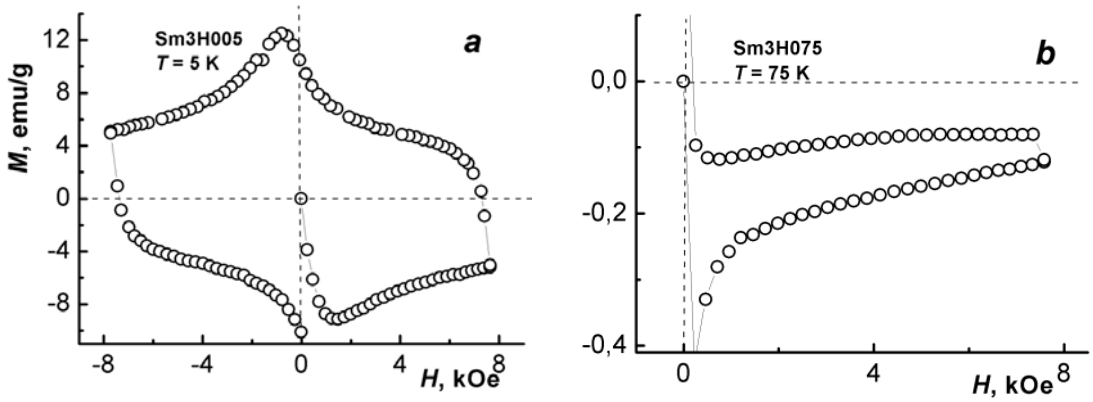

Fig. 5. A loop and a half-loop of magnetic hysteresis in $YBa_{1,90}Sm_{0,10}Cu_3O_{7.07}$ at 5 K (*a)* and 75 K (*b*).

It is well known that type-II superconductors exhibit magnetic hysteresis. Finite resistivity and magnetic hysteresis in these superconductors appear because the motion of flux filaments is pinned by defects such as voids, inclusions, dislocations, grain boundaries, and compositional variations. This pinning results in an irreversibility of metastable states, which manifest themselves in hysteresis. In HTSC ceramics, important factor is the sensitivity of critical current of weak links to local intergrain fields [5]. When the flux filaments depin by thermal activation, or because a current density exceeds some critical value, their motion induces an electric field [6].

The difference between the values of magnetization M (specific moment m) on ascending (M_{asc}) and descending (M_{des}) branches of the hysteresis loop ($\Delta M = M_{asc} - M_{des}$) at a given strength of magnetic field may serve as a measure of pinning efficiency in type-II superconductor and thus assess its practical effectiveness. The critical current density J_c may be estimated in frames of Bean model [7], which assumes that the critical current density does not depend on magnetic field ($J_c(H)$ = const). The value of J_c may be obtained from the following formula:

$$J_c = 15\ (\Delta M/R),\ \text{A/cm}^2$$

where ΔM is the width of the magnetization hysteresis loop ($\Delta M = M_{asc} - M_{des}$) in emu/cm^3; R is the radius of the sample, cm.

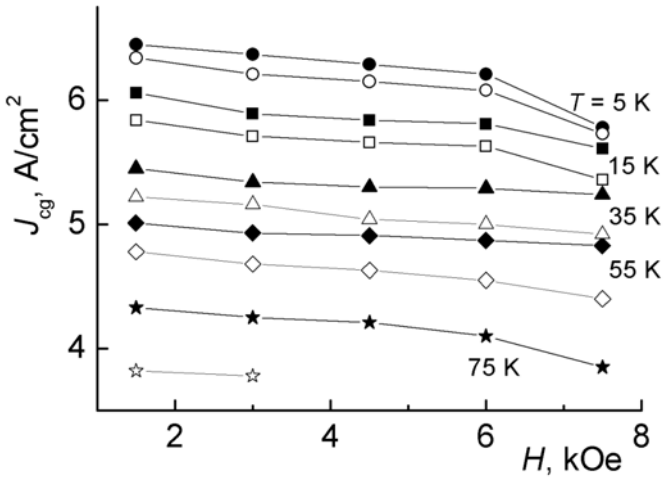

Fig.6. Intragrain critical current densities J_{cg} in samples I (black symbols) and II (open symbols) under different fields H and temperatures T.

In strong magnetic fields this formula may be used for estimation of the value of intragrain critical current density J_{cg} (the current flowing inside the grains [5]) in ceramic samples. In this case R is the radius of a single grain.

It is interesting to compare samples I and II from this point of view. In Fig.6, the calculated values of J_{cg} (in logarithmic scale) are plotted against magnetic field H at different temperatures both for sample I and II. From this comparison, the advantage of HTSC samples fully oxidized with respect to "slow" component of oxygen nonstoichiometry is evident (Fig.6.). Under all fields and temperatures, the critical current densities in sample I are greater approximately by factor of 2 or more than those in sample II. In sample I the density of critical current at 5 K in lower magnetic fields is $J_{cg} \approx 3 \cdot 10^6$ A/cm^2.

Conclusion

Excess oxidation found in cuprates with cation nonstoichiometry due to heterovalent doping may be of practical interest due to somewhat higher both the critical temperature T_c and intragrain critical current density J_{cg} in ceramic specimens.

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В.В.Приседский, С.В.Васильев, Н.В.Маркова, И.В.Мысник, М.М.Ермолов, В.В.Чабаненко СОВМЕСТНОЕ ВЛИЯНИЕ НЕСТЕХИОМЕТРИИ ПО КАТИОНАМ И АНИОНАМ НА СВЕРХПРОВОДЯЩИЕ СВОЙСТВА КУПРАТА 123

Ранее показано, что существует «медленная» составляющая (γ) кислородной нестехиометрии сверхпроводящих купратов 123, легированных редкоземельными элементами. Цель настоящей работы – изучить возможное влияние изменения содержания «медленного» кислорода на электрофизические свойства ВТСП купратов. В магнетометре с вибрирующим образцом измеряли намагниченность легированных Sm образцов $YBa_{1.90}Sm_{0.10}Cu_3O_{6+\delta+\gamma}$ при прямом и обратном сканировании магнитного поля и температуры. Для измерений приготовили из одной и той же партии синтезированного купрата две серии образцов $YBa_{1.90}Sm_{0.10}Cu_3O_{6+\delta+\gamma}$: с максимальной ($\gamma_{max}$ = 0.10) и минимальной (γ_{min} = 0.00) величиной содержания «медленного» кислорода отвечающие соответственно формулам $YBa_{1.90}Sm_{0.10}Cu_3O_{7.07}$ и $YBa_{1.90}Sm_{0.10}Cu_3O_{6.97}$. Изучение магнитного гистерезиса в этих образцах показало, что дополнительное окисление по «медленной» составляющей кислородной нестехиомерии позволяет получить образцы ВТСП с более высокой критической температурой T_c и внутризеренной плотностью критического тока J_{cg} в керамических образцах. Максимальная величина внутризеренной плотности криттока, достигнутая на нетекстурированных керамических образцах, составила $J_{cg} \approx 3 \cdot 10^6$ А/см^2.

Ключевые слова: *высокотемпературный сверхпроводник, купрат, нестехиометрия, магнитный гистерезис.*

В.В.Приседський, С.В.Васильєв, Н.В.Маркова, І.В.Мисник, М.М.Єрмолов, В.В.Чабаненко СУМІСНИЙ ВПЛИВ НЕСТЕХІОМЕТРІЇ ЗА КАТІОНАМИ І АНІОНАМИ НА НАДПРОВІДНІ ВЛАСТИВОСТІ КУПРАТУ 123

Раніше показано, що існує «повільна» складова (γ) кисневої нестехіометрії надпровідних купратів 123, легованих рідкоземельними елементами. Мета цієї роботи - вивчити можливий вплив зміни вмісту «повільного» кисню на електрофізичні властивості ВТНП купратів. У магнітометрі з вібруючим зразком вимірювали намагніченість легованих Sm зразків $YBa_{1.90}Sm_{0.10}Cu_3O_{6+\delta+\gamma}$ при прямому і зворотньому скануванні магнітного поля і температури. Для вимірювань приготували з однієї і тієї ж партії синтезованого купрату дві серії зразків $YBa_{1.90}Sm_{0.10}Cu_3O_{6+\delta+\gamma}$: з максимальною ($\gamma_{max}$ = 0.10) і мінімальною (γ_{min} = 0.00) величиною вмісту «повільного» кисню, що відповідає формулам $YBa_{1.90}Sm_{0.10}Cu_3O_{7.07}$ і $YBa_{1.90}Sm_{0.10}Cu_3O_{6.97}$. Вивчення магнітного гістерезису в цих зразках показало, що додаткове окиснення за «повільною» складовою кисневої нестехіомерії дозволяє отримати зразки ВТНП з більш високою критичною температурою T_c і внутрізеренною щільністю критичного струму J_{cg} в керамічних зразках. Максимальна величина внутрізеренної щільності крітструму, що була досягнута на нетекстурованих керамічних зразках, становила $J_{cg} \approx 3 \cdot 10^6$ А/см^2.

Ключові слова: *високотемпературний надпровідник, купрат, нестехіометрія, магнітний гістерезис.*

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