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# Search for Novel Phases in Y-Ba-Cu-O Family

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**Abstract:** In order to search possible residual minor phases in Y-Ba-Cu-O family, powdered mixtures of $Y_2O_3$ + $BaCO_3$ + CuO and, independently, superconducting compound $YBa_2Cu_3O_{7-x}$ have been treated in evacuated cells and elevated temperatures.$YBa_2Cu_3O_{7-x}$ was reduced to $YBa_2Cu_3O_5$ by use of the special home designed Taconis-Knudsen vacuum device. A subsequent doping by oxygen converts produced insulator $YBa_2Cu_3O_5$ to semiconductor or metal $YBa_2Cu_3O_{5+x}$ ($0<x<0.3$). In addition to $YBa_2Cu_3O_5$, 0.05 volume percent of the minor delafossite phase $Y_2Cu_2O_4$ was being spotted in the powder mixture 1/2 $Y_2O_3$ + $2BaCO_3$+$6Cu_2O$, heated up to 818 °C in an inert gas atmosphere. An attempt to prepare the insulating bulk delafossite samples was successful, and subsequent doping by oxygen produces novel metallic phases.

**Keywords:** thermo-acoustic resonator; delafossites; spin-charge separation; spinons; holons

**PACS:** 74.70.Ya; 74.30.Ci

## Introduction

The discovery of superconductivity (SC) by Chu and co-workers [1] 1987. in a mixed compound $Y_{1.2}Ba_{0.8}CuO$, and indicated by transition temperature $T_c$ = 93 K, was followed by an announcement [2] suggesting a possible appearance of even higher SC transition temperatures, approaching the room temperature (RT). Cava and co-workers [3] promoted the formula of the novel superconductor $YBa_2Cu_3O_{7-x}$ (Y-123). The present author reported resistive transitions at 210 K indicated by small diamagnetism [4,5].Common to worldwide appearances of superconductivity near RT was the poor reproducibility and stability of the evaluated data. The probable reason is very small fraction of the minor phases which must be traced and recognized in the preparation methodology. SC transition temperature of $YBa_2Cu_3O_{7-x}$ decreases by removal of oxygen until, for $x$ >0.7, material becomes an insulator indicated by the tetragonal crystal lattice, and unit cell dimensions a = b = 0,38570 nm, c = 1,18194 nm [6].

Only scarce theoretical work was being put forward on possibility of very high SC transition temperatures. Little promoted an idea [7] how organic linear chains may obey superconductivity at temperatures higher than dreamed 30 K , and further concepts published in scientific literature operated with quasi-one-dimensional conductivity, since it is evident that Cooper coherence can't be established at high temperature in 2D and 3D conducting systems.

The question arises here on the possibility of lower oxidation states in Y-123, say $1<x<2$, while the crystal structure could be isomorphic with the original tetragonal phase. In this paper it is described a preparation of the novel metal $YBa_2Cu_3O_{5+x}$ (Y-5).In addition to Y-5, it was found the next minor phase $YCuO_2$ in Y-Ba-Cu-O mixtures, and its structural, resistive and magnetic properties are reviewed.

## Experiments

In order to trace the low concentrated minor phases in Y-Ba-Cu-O family, the standard preparations of Y-123 in the flowing oxygen atmosphere at 935 °C, must be replaced by more unconventional methods, which include treatment in an evacuated cell and firing temperatures ranging from 500-1100 °C. The powders of prepared compounds were pressed into pellets 8 mm in diameter and 0.8-1 mm thick, and in order to measure electric resistance, four gold wires, 100 microns in diameter, we pressed together with the powder as shown in the inset of Figure 8a.

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**$YBa_2Cu_3O_{5+x}$**

Two oxygen atoms were removed from the Y-123 (x = 0.16) pellet by use of the vacuum sublimation device designed in this laboratory and schematically presented in Figure 1.

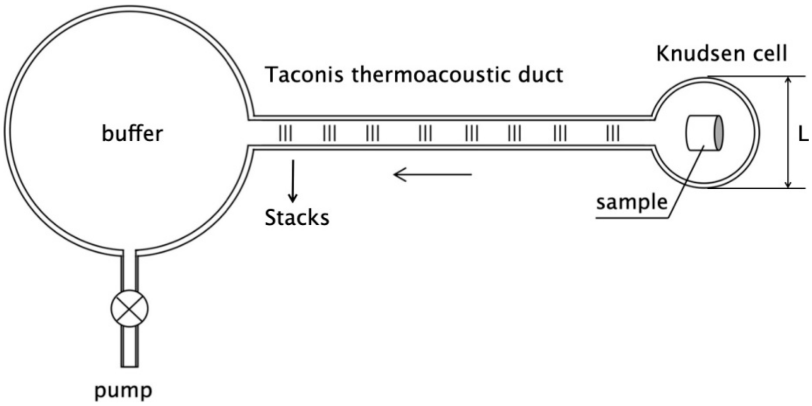


**Figure 1.** Schematic principle of a thermo-acoustic resonator which resonates between Taconis thermo-acoustic duct and Knudsen cell.

The thermo-acoustic engine resonates between Taconis thermo-acoustic duct [8] and Knudsen cell, the latter held at 645 °C, while buffer is at RT. Gas dynamics in a Taconis duct is governed by two parameters; dynamic gas viscosity $\nu = \mu/\rho$ indicated by a viscous depth $l = (2\nu/\omega)^{1/2}$ and thermal diffusivity of the gas in the duct given by $k = \lambda/\rho \cdot c_p$. $\lambda$, $c_p$ and $\rho$ are thermal conductivity, specific heat and gas density respectively. The ratio of a dynamic viscosity and thermal diffusivity defines Prandtl number governing the sublimation efficiency from the sample. The Taconis gas density stacks are visualized in the duct.

The practical performance of the thermo-acoustic resonator is visualised in Figure 2. Sample is positioned in the cell 1 and the pumping was proceeded through screw thread 2, funnelled to a coaxial duct between sample holder 3 and outer tube 4. The diameters between outer 4 tube and inner sample holder 3 differ 0.14 mm and define the cross-section of the duct. The volume of the Knudsen cell is 0.8 $cm^3$ and it resonates with Taconis oscillations, giving rise to the pressure fluctuations strong enough to drain oxygen from the sample. Obviously, molecular velocities v = $(2\delta p/\rho)^{1/2}$, driven by pressure oscillations in a small density range $\delta p$, are in the supersonic regime indicating that the strong sublimation occurs. The pumping path in the coaxial duct terminates in a vacuum buffer and dynamic pressure ~ 0.15 mbar in the buffer was adjusted by a fine needle valve. The temperature was monitored by use of the type K thermocouple 5. An additional adjusting parameter is provided by the fraction of the Taconis coaxial duct exposed to the hot zone of the oven. The Knudsen cell was maintained at constant temperature 645 °C and enhanced pressure oscillations in the cavity favour strong reduction of oxides. For instance, copper oxide CuO was reduced to the pure copper already at 332 °C. The resonant frequency of 11,2 kHz was measured by use of a hot wire anemometer 6 assembled from the platinum wire 25 microns in diameter, and fixed in the buffer interior.

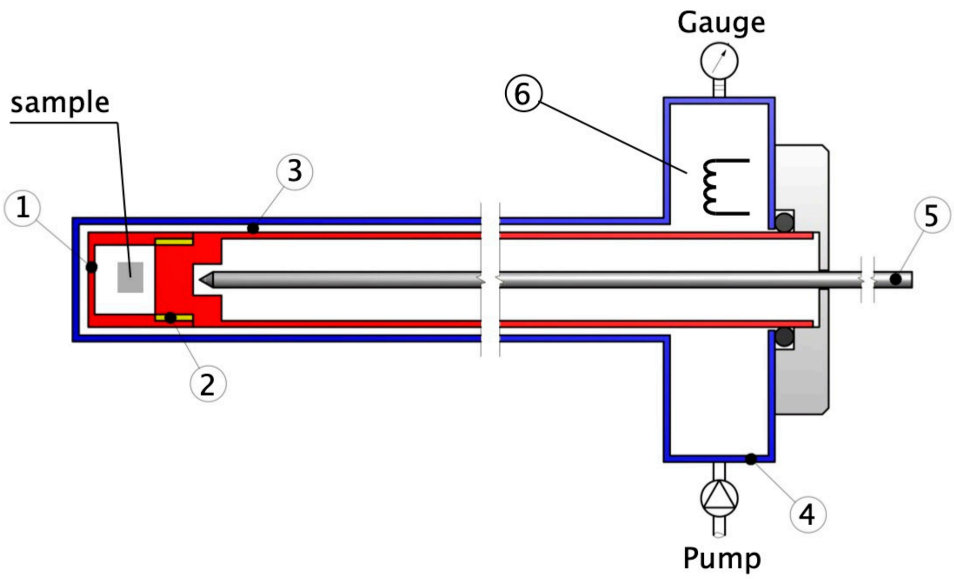


**Figure 2.** Technical performance of the thermo-acoustic resonator.

The reduction of Y-123 superconductor was monitored by weight, and XRD data are presented in Figure 3. Refinement gives the dimensions of the tetragonal cell a = b = 0,38605 nm and c = 1,18450 nm. The samples are indicated by yellow colour, and an additional evaluation of the oxygen content was performed by reduction in hydrogen atmosphere. The final result was $YBa_2Cu_3O_{5\pm0.06}$. When exposed to free air atmosphere Y-5 absorbs the oxygen and, in the course of one month of the exposure, it converts to $YBa_2Cu_3O_{5,14}$.

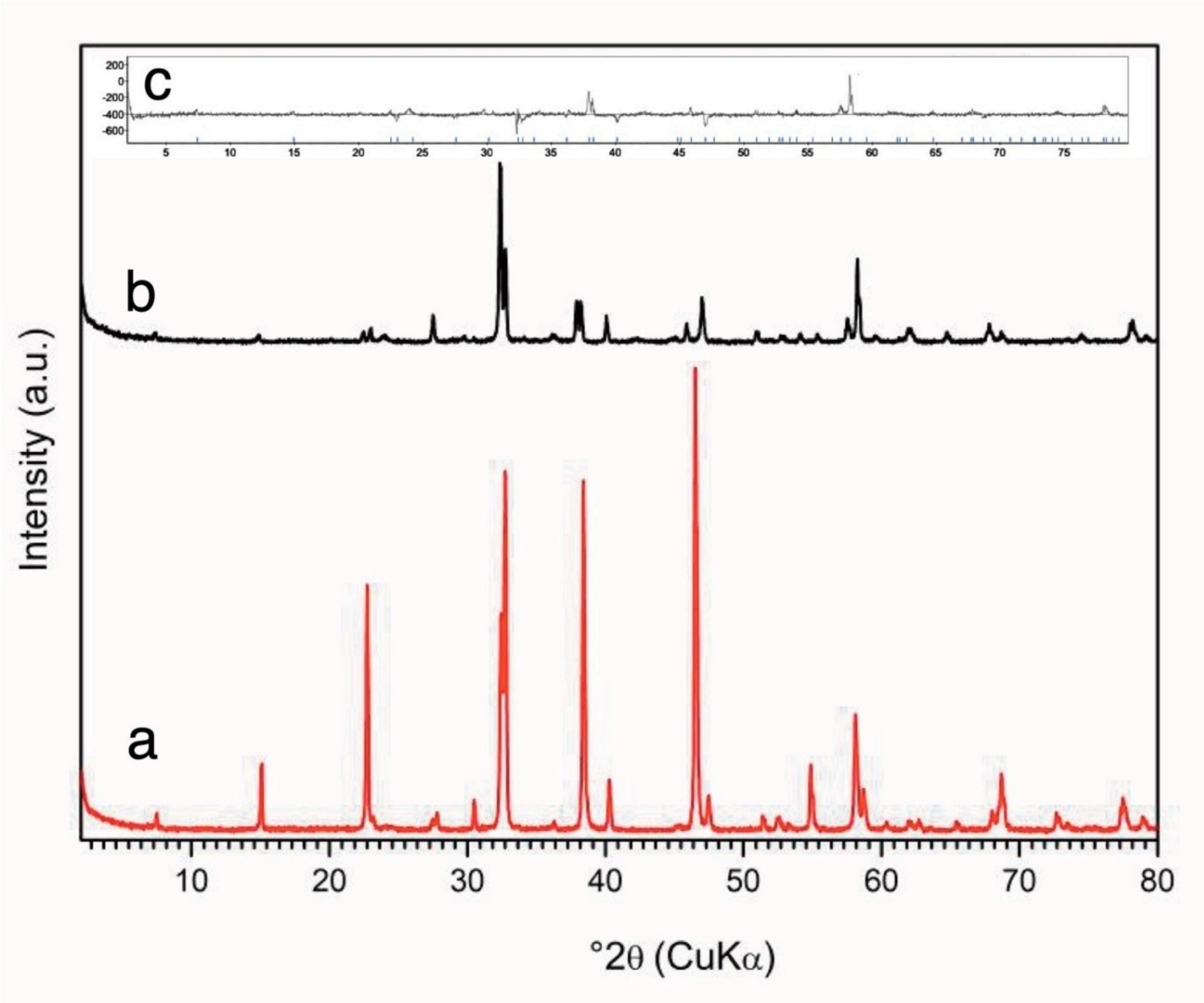


**Figure 3.** X-ray diffractograms: (a) the superconducting sample Y-123, (b) $YBa_2Cu_3O_5$ (Y-5) obtained by removal of two oxygen atoms from the same sample Y-123, (c) Y-5 structure refinement.

Doping of the pellet $YBa_2Cu_3O_5$ by oxygen was proceeded in a calibrated alumina cell. In an independent heating stage cell was filled by argon gas, in order to evaluate an increase of the pressure by heating and to trace the possible degassing from the ceramic background. Oxygen pressure was measured by use of absolute capacitance gauge of sensitivity better than 0,1 mbar.

The oxygen doping is presented in Figure 4, and starting oxygen pressure at RT was 50 mbar (a).The attached straight line shows an increase of the pressure as a result of the cell heating, prior to absorption which starts at 292 °C. It is indicative that the slope of the temperature dependent pressure after absorption differs from the initial one and an additional absorption step is visible at 632 °C, appealing for second minor phase in Y-5.Release of adsorbed oxygen starts at 825 °C and additional pressure, above linear straight line results from the partial deterioration of the unit cell Y-5.Temperature dependence of the oxygen pressure by cooling to RT is shown in curve (b), while yellow pellet becomes black. Final oxygen content of 2,625 moles in the pellet was evaluated by weight and by reduction in 2 bar hydrogen atmosphere at 410 °C.

In the next preparation $YBa_2Cu_3O_{5,32}$ was produced, and temperature dependence of the resistance, measured in 10 mA AC current 20 Hz by use of the lock-in amplifier is shown in Figure 5. It falls down at 41°C and magnified potion between –10 and +10 °C is shown in the inset. Amplification of the lock-in transformer is frequency dependent for very small resistances measured, and pellet of the silver, and similar size, was used as an etalon for calibration on frequency. Comparatively high measuring current lifts the sample resistivity to $10^{-5}$ Ωcm, while application of 1

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mA results in the resistivity less than $10^{-6}$ Ωcm. Extrapolation to zero current gives $0{,}17\cdot10^{-6}$ Ωcm at ice point.

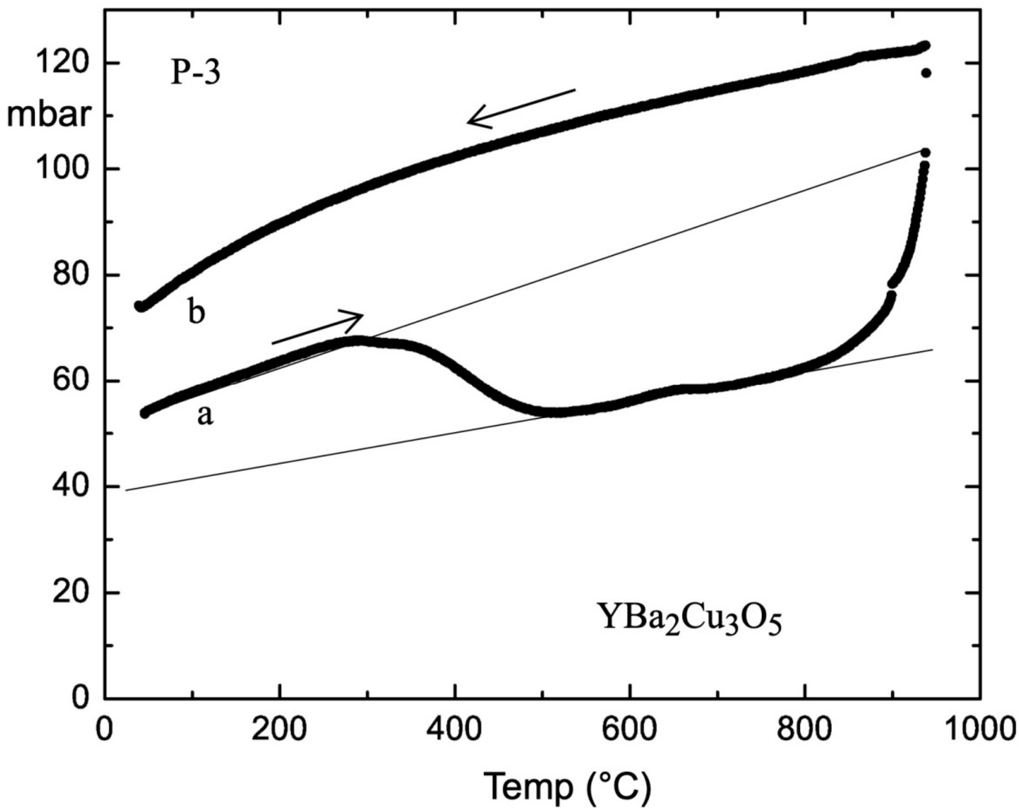


**Figure 4.** Temperature dependence of the oxygen pressure in the cell containing the pellet of $YBa_2Cu_3O_5$.

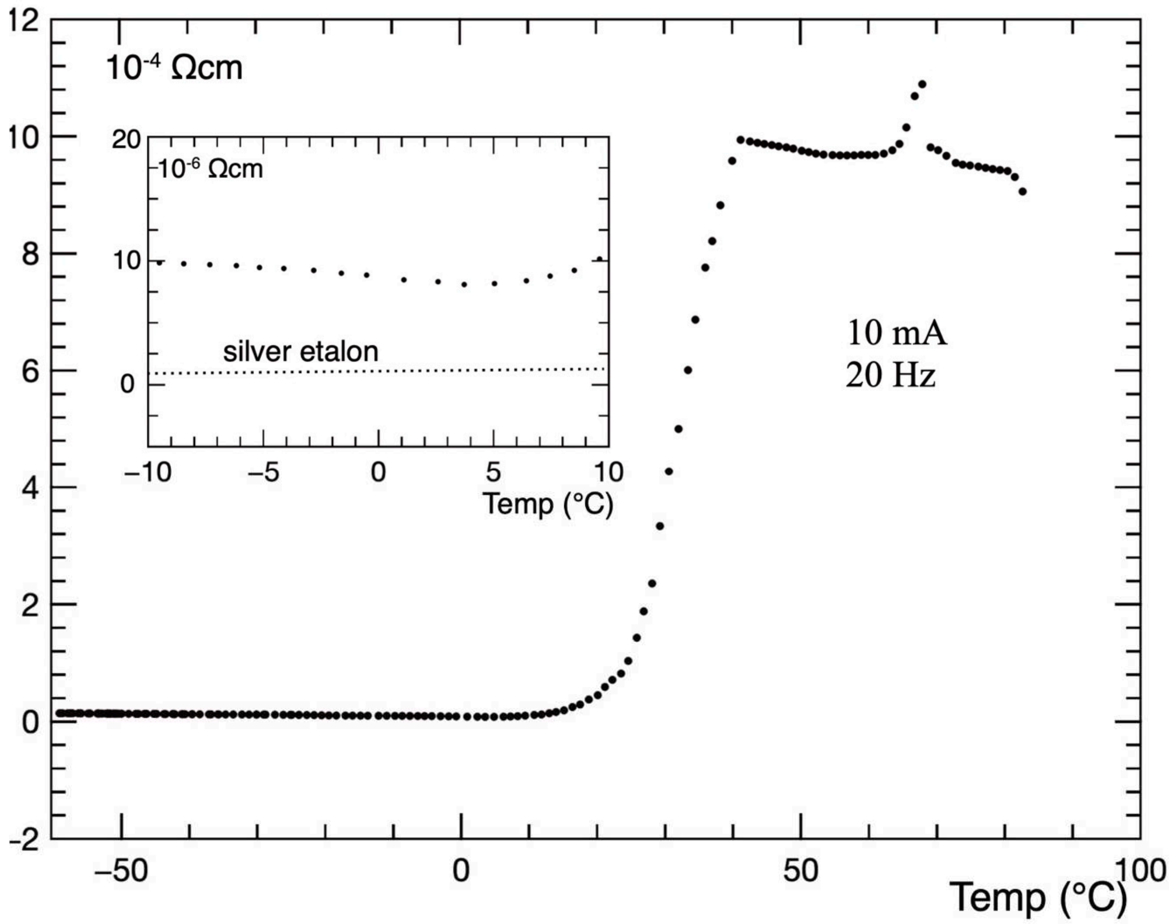


**Figure 5.** Temperature dependence of the electric resistance of $YBa_2Cu_3O_{5,32}$ measured at 20 Hz and 10 mA by lock-in amplifier. Inset shows the magnified data in the temperature range –10 °C + 10 °C.

The measurement of AC magnetic susceptibility of $YB_2Cu_3O_{5.25}$ was performed by use of a high resolution CryoBIND Research susceptometer. Real (black) and imaginary (red) parts are shown in Figure 6.The mass of the sample was 57 mg. AC field was 0,75 Oe (RMS),frequency 231 Hz, and superimposed DC field 44 Oe. The data appeal for two diamagnetic phases. One phase is indicated by temperature dependent susceptibility decreasing by cooling from +11 °C, and its volume fraction is estimated to be 0,05 percents. Second phase is $YBa_2Cu_3O_{7-X}$ remain after incomplete draining in the Knudsen cell, and its volume fraction is 0,25 percents.

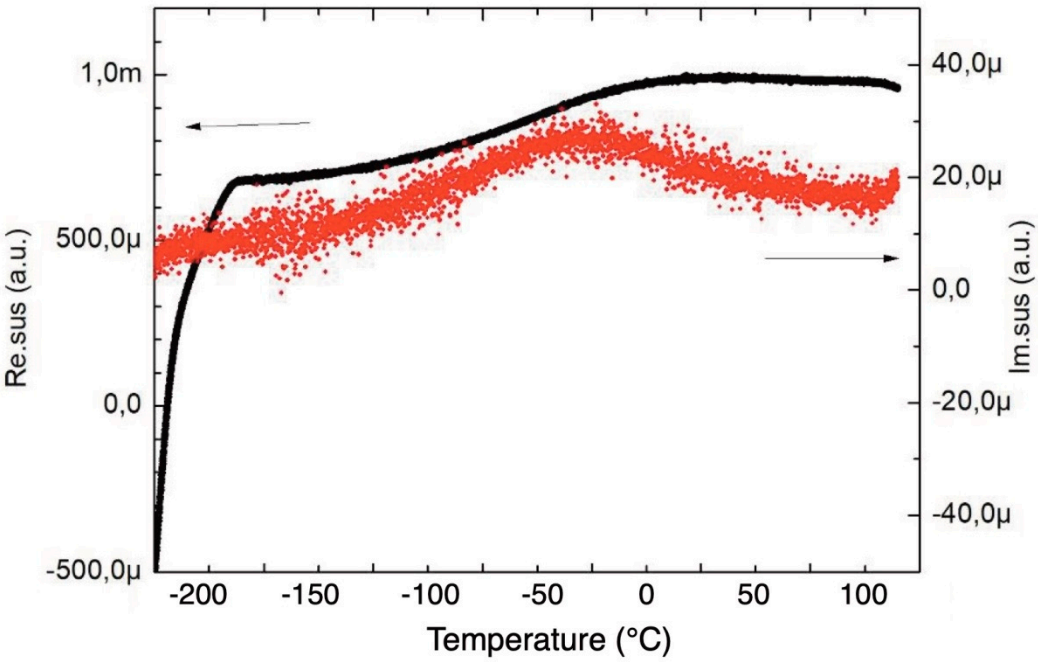


**Figure 6.** Temperature dependence of the real (black) and imaginary (red) part of the AC susceptibility of the oxygen doped $YBa_2Cu_3O_{5,25}$. Left to the black curve, it is visible 0,25 volume percent of superconducting Y-123, remained after thermo-acoustic reduction.

An important achievement of these experiments is a fair reproducibility of the measured data. However, an appreciable increase of the diamagnetic fraction was not observed during the preparation, and this in turn calls an attention that yellow phase may not be a carrier of the diamagnetic susceptibility above 93 K. Moreover, although XRD stressed the iso-structural properties with $YBa_2Cu_3O_6$, shown in Figure 3 several additional and indicative diffractions seem to appear.

**Delafossite $Y_2Cu_2O_{4+\delta}$**

Non reacted mixture Y-123 was heated and analyzed by simultaneous differential scanning calorimeter (DSC) and thermogravimetry (DTG) in an inert gas atmosphere. The measured data, shown in Figure 7, stress endothermic features at 818 °C, 926 °C (Y-123 phase), 1028 °C (green phase $Y_2BaCuO_5$), and 1175°C.The endothermic peak at 818 °C is indicated by absence of $BaCO_3$ decomposition. Obviously, it is going on a reaction with no barium involved, which sounds for group of oxides $Y^nCu^nO_x$ refereed in the literature as delafossites. The lowest member ishexagonal $YCuO_2$ firstly synthesized by Ishiguro and co-workers [9], and later examined by Aride and co-workers [10].

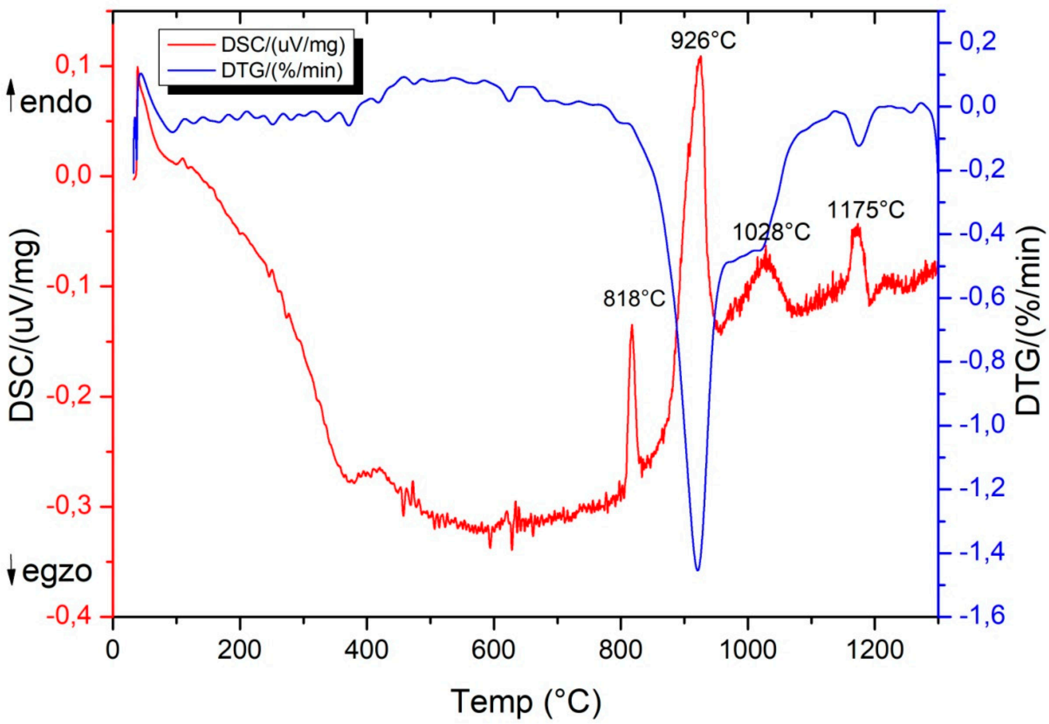


**Figure 7.** DSC-DTG record of the previously unfired mixture $1/2Y_2O_3$+$2BaCO_3$+$Cu_2O$ in argon atmosphere. Endothermic feature at 926 °C corresponds to formation of the tetragonal Y-123 phase.

Starting powder components for preparation of $Y_2Cu_2O_4$ are $Y_2O_3$+$Cu_2O$, pressed in pellets and fired for 24 hours in vacuum at 818-820 °C. Pink coloured pellet becomes reddish-black and insulating, while XRD record confirms the presence of $YCuO_2$,non reacted $Y_2O_3$ and elementary Cu. Preparations at 0,5 and 1 bar oxygen result in reddish and green/grey colours respectively, both species being insulators. Hexagonal cell lattice parameters are a = 0,35206 nm, and c = 1,1418 nm.

Next experiments were focused on the insulating samples $Y_2Cu_2O_4$ doped by comparatively small oxygen pressures. Figure 8 shows a gradual decrease of the resistivity, measured in air, with increasing oxygen pressure in the reaction cell. The pronounced maxima of resistivites are observed at –21 °C and –53 °C for oxygen pressures 2,4 and 10,2 mbar respectively.

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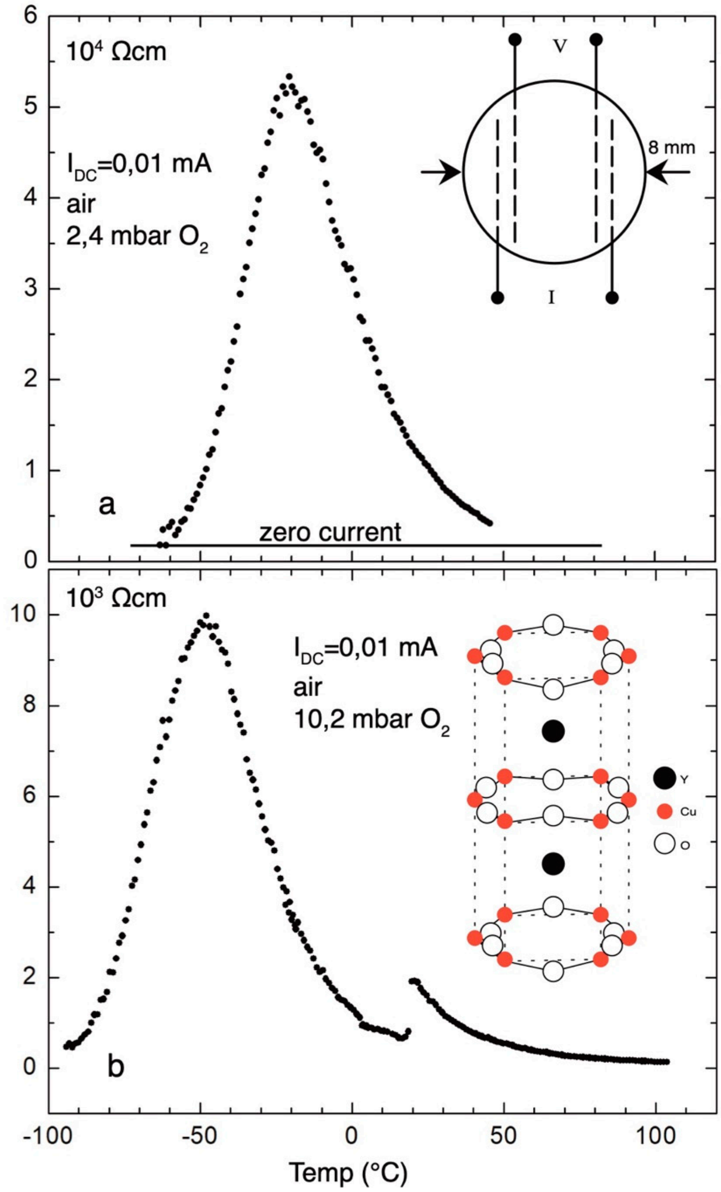


**Figure 8.** Temperature dependence of the resistivity of $Y_2Cu_2O_4$ , measured in air, after annealing in oxygen atmosphere: (a) 2,4 mbar, and inset shows the sample pellet with impressed 100 microns gold wires, (b) 10,2 mbar, and inset presents the hexagonal structure of $Y_2Cu_2O_4$ as reported by Ishiguro and co-workers.

It was observed that annealing near 40-50 mbar oxygen results in the lowest resistivities, order of $10^{-4}$ Ωcm at ice point, and by further increase of the oxygen pressure, higher than 150 mbar, samples become gradually again insulators. In both extreme cases valency of copper is uniform; $Cu^{+}$ in zero pressure annealing and $Cu^{2+}$ in 1 bar. Mixed valency state $Cu^{+}/Cu^{2+}$, as precondition for a conductivity, is established for oxygen pressures between 0,01 and 0,5 bar. Depending on the annealing pressure, pellets are differently coloured, which appeals for more complex pressure-temperature phase diagram.

The next doping pressure , dependent on temperature, is shown in Figure 9. Starting pressure at RT was 100 mbar. In order to minimize the background increase of the pressure due to the heating, pressure cell was externally buffered. The absorption starts at 395 °C and finishes at 587 °C. In order to eliminate contribution of the oxygen adhered on the grain boundaries the pressure cell was evacuated prior to cooling to RT, and it is visible an increase of the released oxygen at temperatures

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approaching RT. The remaining oxygen pressure in air was 38 mbar, confirmed also by a weight control.

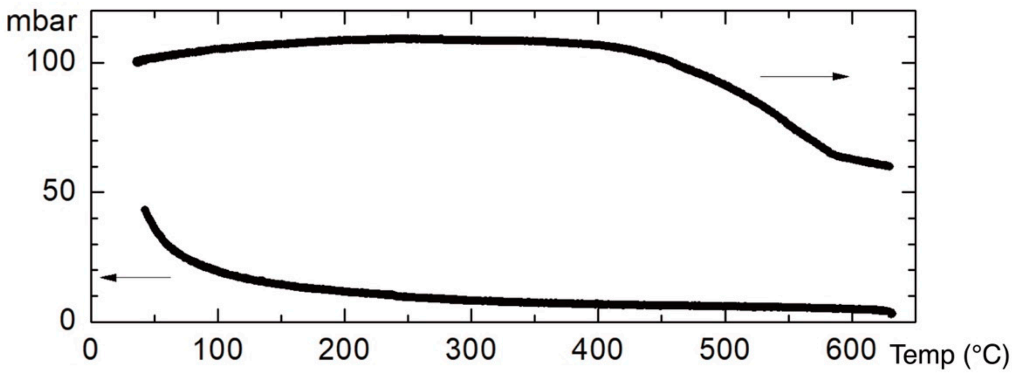


**Figure 9.** Doping of $Y_2Cu_2O_4$ by oxygen, and cooling to RT after evacuation.

Figure 10 shows the temperature dependence of the electric resistivity measured in air, after annealing in oxygen pressures at temperatures up to 645 °C, as presented in Figure 9, and it decreases comparatively slow by cooling due to high measuring current 10 mA. Resistivity falls below $10^{-6}$Ωcm at temperature less than -100 °C.

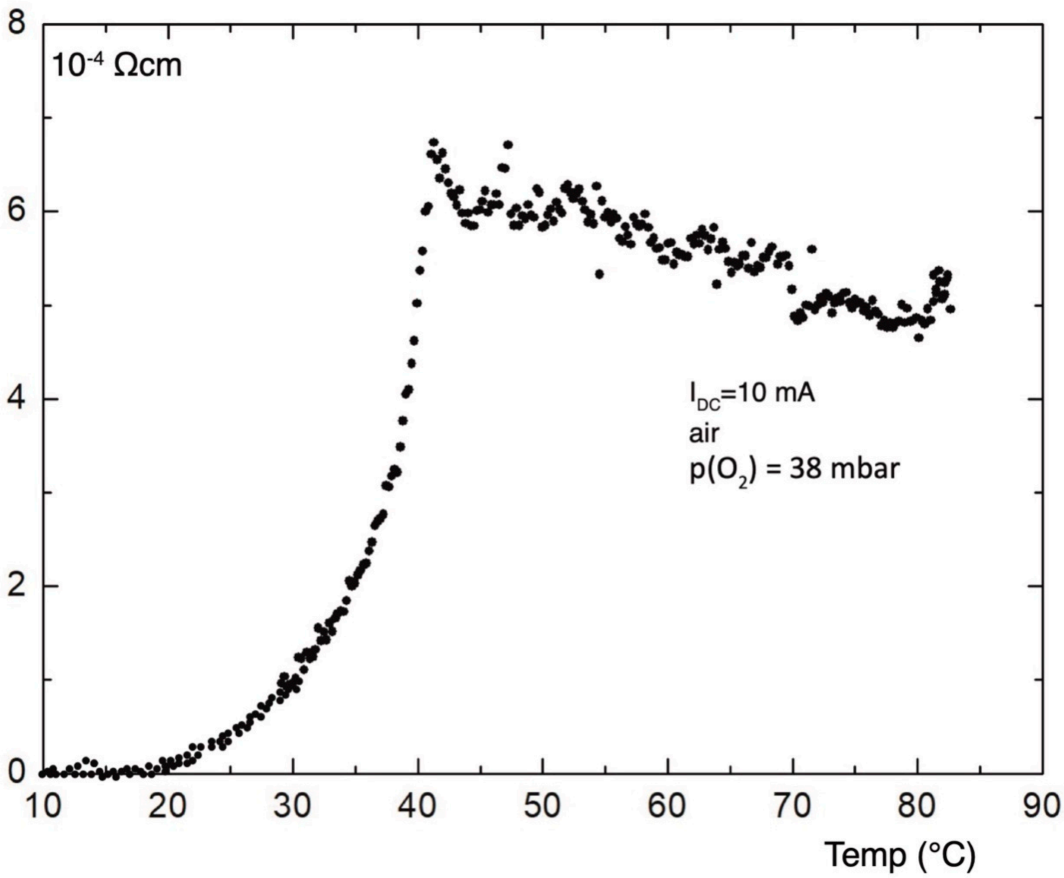


**Figure 10.** Temperature dependence of the resistivity, measured in air, of the sample $Y_2Cu_2O_4$ after annealing in 38 mbar oxygen atmosphere at 645 °C.

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AC magnetic susceptibility of the pellet presented by resistivity, shown in Figure 11, was measured in air by use of primary and two secondary coaxial coils. The signal from two secondary coils was compensated, when both empty. Certified pellet of High Tc superconductor $GdBa_2Cu_3O_{7-X}$, diameter 10 mm and thickness 1 mm, was used as an etalon. Etalon diamagnetism, at $LN_2$ temperature 77 K, is SI = – 0.97.

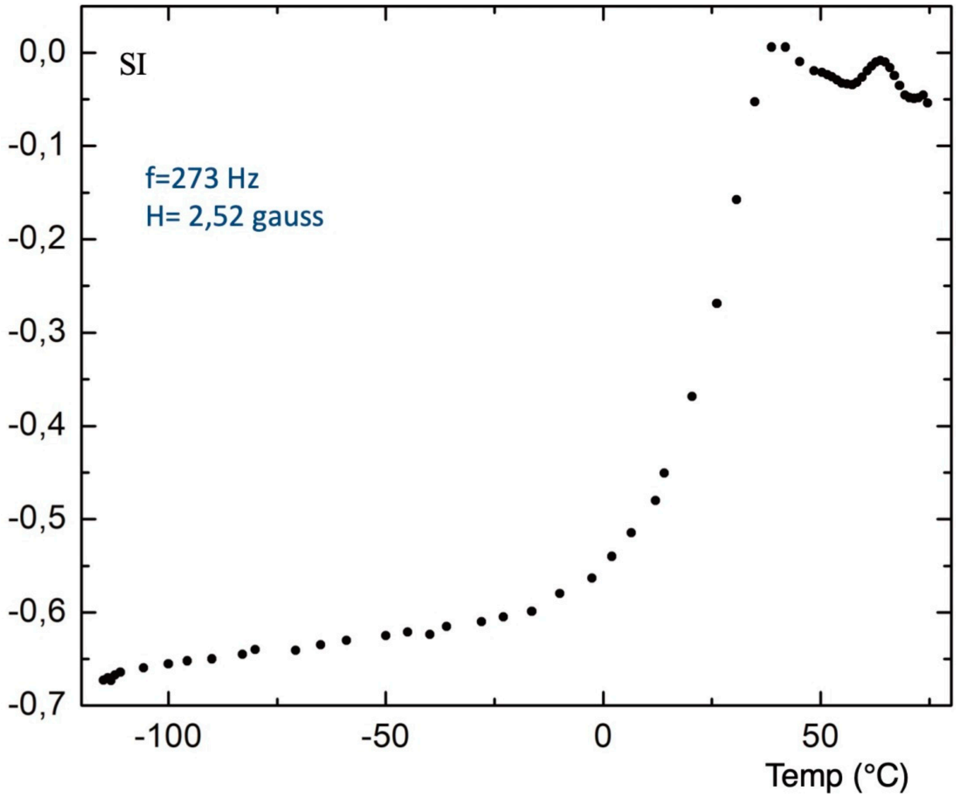


**Figure 11.** Temperature dependence of magnetic AC susceptibility of the pellet $Y_2Cu_2O_{4+\delta}$ used in electric resistance measurement and shown in Figure 10. Pellet was fixed in a secondary coil balanced with other identical coil in secondary circuit.

**Discussion**

Two compounds $YBa_2Cu_3O_5$ and $Y_2Cu_2O_4$ are insulators containing only $Cu^+$ cations embedded in mutually orthogonal $Cu^+$–O–$Cu^+$ chains. Absorption of oxygen converts partly $Cu^+$ to $Cu^{2+}$ creating mixed valency state indicated by good conductivity of electricity proceeded along the polarized chains, which is followed by transitions to low resistivity state near RT. The question arises, why diamagnetic contribution, in predominant mono-phase Y-5, presented in Figure 6, is still small. More like, it seems that it arises from $Y_2Cu_2O_2$ as a minor phase in Y-5. However, the premature exclusion of resistive and magnetic transitions in Y-5 doesn't seem to be productive, while relatively high amount of absorbed oxygen suggests the promising set of novel experiments.

In some aspects insulating $Y_2Cu_2O_4$ is similar to $La_2CuO_4$ which becomes superconducting when doped by oxygen [11,12,13], and both oxides are very sensitive on doping $\delta$. Even small exposure to oxygen reduces dramatically electric resistivity, as it is shown in Figure 8. A pronounced maximum of the temperature dependent resistivity reflects the competition of magnetic (spinon) and electric (holon) degrees of freedom expressed in $t-J$ Hamiltonian involved in modern models of spin-charge separation. In classic theories of the superconductivity, like BCS, Cooper instability drives the electron pairing at temperature $T^*$ ; $\ln(kT^*/p_F v_s) = -p_F \cdot v_s / J$. $p_F$ and $v_S$ are Fermi surface momentum and spin velocity respectively. At higher doping densities, spinon and holon velocities are equal $v_h = v_s = J/p_F$ and maximum of temperature dependent resistivity occurs at $kT^* = J$. $J$ is linear dependent on small doping $\delta$ [14],and expression for the Cooper instability gives maxima in Figure 8.

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Spin-charge separation was firstly observed in a one-dimensional compound $SrCuO_2$ [15,16]. Cu-O distances in $Y_2Cu_2O_4$ are 3,52 Á, which is considerably higher than those in insulating $SrCuO_2$ (0,16 nm), and Y-5 (0,193 nm). Consequently, spinon and holon velocities will be higher in smaller Cu-O chain density [17], which is followed by smaller charge transfer gap. Spin-charge separation embodied in t-J Hamiltonian indicates strong competition between the superconductivity and insulating state. Competition is the usual guide, as a home recipe, for search of new superconductors presuming insulators as possible candidates. $SrCuO_2$ is not superconducting, indicating that more complicated connection of the superconductivity and spin charge separation must be considered. In order to put forward further analyses it may be customary to reduce partly $SrCuO_2$ by above described thermo-acoustic resonator and induce the mixed valency state.

## Conclusions

Two insulating phases, $YBa_2Cu_3O_5$ and $Y_2Cu_2O_4$ which appear as minor components in the preparation of $YBa_2Cu_3O_{7-x}$ superconductor were focused and independently prepared. Doping by oxygen results in quasi-one-dimensional conductors indicating that some resistive and magnetic properties call attention for a novel superconductivity.

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