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Some diffusive properties of oxygen in Y-Ba-Cu-O systems

D. Djurek ⁽¹⁾, V. Manojlović ⁽¹⁾, Z. Medunić ⁽¹⁾, M. Prester ⁽²⁾, E. Babić ⁽³⁾ and K. Zadro ⁽³⁾

⁽¹⁾ Volta Applied Ceramics, 41000 Zagreb, Croatia, Yugoslavia

⁽²⁾ Institute of Physics of the University of Zagreb, 41000 Zagreb, Croatia, Yugoslavia

⁽³⁾ Department of Physics, Faculty of Natural Sciences, 41000 Zagreb, Croatia, Yugoslavia

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Abstract. — We have studied the diffusive properties of oxygen in Y-Ba-Cu-O systems at 940 °C by measurements of the resistive response time τ of the samples subjected to the step-like increase of the oxygen pressure $\Delta p_{O_2} \sim 1$ to 5 bars. The superconducting (SC) transition widths ΔT_c plotted *versus* inverse diffusion constant $D^{-1} \sim \tau$ obey the universal linear dependence. The characteristic protruded tail of the real part of AC susceptibility which exhibits the feature at 86 K is absent in samples with the nominal composition $Y_3Ba_3Cu_6O_x$ (Y-336) in the regime $\tau < 3$ s as result of weakly connected grains of $YBa_2Cu_3O_{7-\delta}$ (Y-123) nucleated from decomposed Y-336 phase.

Introduction.

The oxide superconductor $YBa_2Cu_3O_{7-\delta}$ (Y-123) is still the subject of an intensive research, because of comparatively simple preparation procedure and attractive extension of conventional ceramic properties to superconductivity. There is less evidence in scientific literature on the correlations of physical properties recorded at 900-940 °C and SC data observed below 90 K. The commonly accepted result that O_2 favours the SC properties in Y-Ba-Cu-O systems is less evident by *in situ* recording of oxygen diffusion during the annealing at high temperatures and diffusivity data don't form a coherent picture in detail with considerable differences existing from group to group [1].

While thermogravimetric (TGA) analysis offers an insight in the amount of captured or released oxygen in the sample the diffusive properties of oxygen are less accessible by TGA.

Recently we have introduced [2] the measurements of the electrical resistance (R) of samples during the heat treatment and reported the close correlation of R with the mass of absorbed or released O_2 in Y-123. The time dependence of R may elucidate the mechanism of the diffusion of O_2 and/or O. In this paper we report the results of the measurements of the resistive response in the samples subjected to a step like increase of O_2 pressure Δp_{O_2} (~ 0.5 s for 90 % of Δp_{O_2}) at sintering temperature (~ 940 °C) after sintering procedure (~ 12 h) has been finished. An increase Δp_{O_2} from 1 to 5 bars results in the decrease of R from

R_0 in time and this decrease can be fitted to an exponential dependence $\delta R = (R_0 - R_\infty) \exp(-t/\tau)$. The temporal and spatial dependence of oxygen concentration (n) in thin sample of the area S is governed by the diffusion equation $\delta n/\delta t = D \delta^2 n/\delta x^2$ with diffusivity D related to ($\tau = S/D$).

The diffusive properties of oxygen in Y-Ba-Cu-O can be considered in two respects. Firstly, intragrain diffusion is mainly governed by oxygen-oxygen repulsion energy $E_r \sim 0.16$ eV [3] which contributes to diffusion times $\tau \sim 10^{-7}$ s [4] according to expression $\tau = \tau_0 \exp E_r/kT$ with $\tau_0 \sim 8 \times 10^{-13}$ s [5]. Otherwise the activation energy E_r which corresponds to the site oxygen removed from the grain boundaries (GB) to the interior is $E_r \sim 2 - 2.5$ eV [6] with corresponding diffusion times $\tau > 10$ s.

In fact, diffusion rate $\delta n/\delta t$ of the oxygen in Y-123 is related to the strain rate $\delta \varepsilon/\delta t$ since strain fluctuations $\delta \varepsilon$ are suppressed by removing of variations δn of concentration n_0 according to Nabarro-Herring expression $\delta n/n_0 = \omega_0 \delta \varepsilon/kT$. ω_0 is the lattice site volume $\omega_0 \sim 11 \text{ \AA}^3$ for unoccupied vacancy or the volume $4 \pi r_0^3/3$ for oxygen occupied vacancy site. r_0 stands for the effective distance of long-range elastic interaction and exceeds at least 20 atomic coordination shells [7].

Experiment.

Y-Ba-Cu-O samples were prepared from powders Y_2O_3 , CuO and $BaCO_3$ mixed in an agat mortar and fused at 940 °C for 24 h, usually in two heat cycles, in order to complete the solid state reaction. After cooling to room temperature (RT) the fused compound was reground and subsequently compacted in pellets ($S = 0.2-0.4 \text{ cm}^2$, 200 μ in thickness). The sintering was performed at 940 °C in air after which the resistive response to $\Delta p_{O_2} = 5$ bars was recorded. By cooling to RT we additionally annealed the samples at 430 °C for 12 h in the flowing O_2 (~ 1 bar) in order to remove the variations of O_2 concentration among different samples as a result of irreproducibility of the furnace cooling rate.

The powders of Y-123 were compacted with different pressures in order to provide the different time constants at 940 °C. The respective compaction pressures at RT for samples a, b and c with resistive SC transitions shown in figure 1 were 0.8 GPa, 3.1 GPa and 8.2 GPa. The heating up to 940 °C and annealing for 12 h resulted in three different values of diffusion constants D as it is shown in figure 2.

The fusion of Y-336 differs in some respects from Y-123. Iqbal and coworkers [8] reported that single phase Y-336, as previously reported by Raveau and coworkers [9] can't be obtained as a stable one by the solid state reaction and authors suggested sol-gel method as preparation procedure for obtaining stable Y-336.

We fired the powder mixture of nominal composition $Y_3Ba_3Cu_6O_x$ at 880 °C for 20 h and X-ray diffractograms taken on samples quenched to RT from 880 °C by simple pulling from the furnace reveal the presence of Y-336 phase characterized by $hkl = 111$ ($2\theta = 24^\circ$) diffraction. The reground and compaction with subsequent sintering for 12 h at 940 °C in air revealed a comparatively small time constants ($\tau = 2-4$ s) recorded at 940 °C and cooling to 430 °C with subsequent annealing at this temperature in 1 bar of flowing O_2 confirmed the presence of Y-123, Y_2BaCuO_5 (insulating phase) and CuO. To the lowest $\tau = 2$ s corresponds comparatively narrow resistive transition width $\Delta T_c = 0.4$ K (inset of Fig. 3). In addition to low resistive ΔT_c the diamagnetic transition in Y-336 is qualitatively different from that in Y-123 (Fig. 3). The transition is smooth with an absence of the protruded tail and nearly 80 % of transitions is finished in 1.5 K.

The samples of mixed phase $Y_{1.2}Ba_{0.8}CuO_x$ a' , b' and c' were prepared by application of different compaction pressures to the powders with respective values 1.4 GPa, 2.2 GPa and

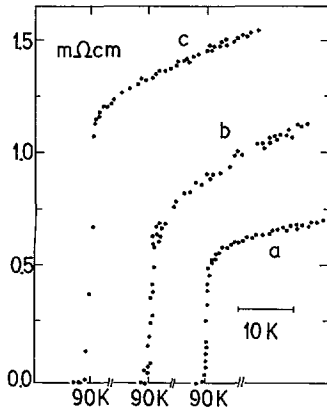


Fig. 1.

Fig. 1. — Resistive transitions to SC state in samples Y-123 subjected to three different compaction pressures : a ($p = 0.8$ GPa), b ($p = 3.1$ GPa), c ($p = 8.2$ GPa).

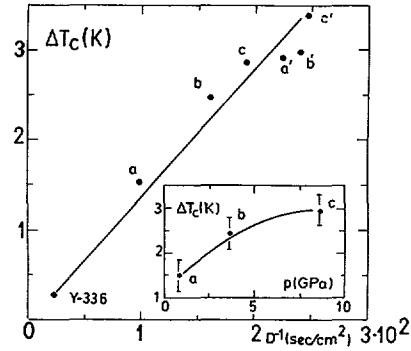


Fig. 2.

Fig. 2. — SC transition width ΔT_c plotted versus inverse diffusion constant D^{-1} . The inset shows the dependence of ΔT_c in Y-123 on compaction pressure as referred in figure 1.

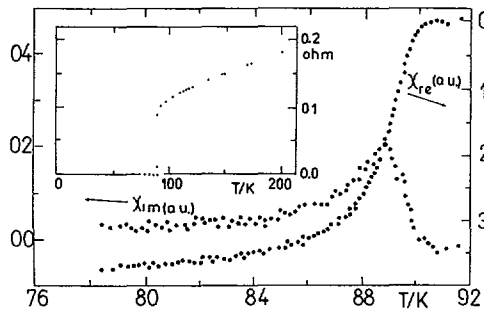


Fig. 3. — Diamagnetic transition in Y-336 decomposed in real part χ_{re} and imaginary part χ_{im} . The inset shows the resistive transition in Y-336 to SC state.

3.8 GPa. The corresponding D^{-1} and transition widths are plotted in figure 2. Similarly as in the case of Y-123 ΔT_c and D^{-1} are increasing functions of applied pressure.

Discussion.

An increase of τ with applied uniaxial pressure in Y-123 for $p > 10$ kbars may be explained by appearance of dislocation creep commonly introduced by twins on twin-twin and twin-grain boundary intersections. An importance of twins as a possible dislocation source in Y-123 was stressed recently [10].

While at high temperatures ($T > 0.5 T_m$; T_m is melting temperature of Y-123) and low normalized stress σ/μ (μ is shear modulus) the dislocation strain rate $\dot{\epsilon}_{DISL}$ is dominated by lattice diffusion $\dot{\epsilon}_{DISL} \sim (\sigma/\mu)^n$ [11] (n is an integer) at low temperatures ($T < 0.3 T_m$) and high stresses ($\sigma/\mu > 10^{-3}$) the dislocation strain is smaller and varies as $\dot{\epsilon}_{DISL} \sim (\sigma/\mu)^{n+2}$

An application of stress at $T < 0.3 T_m$ locks the intergrain viscosity (Cottrell type of lock) up to sintering temperatures with corresponding suppression of oxygen diffusivity.

The comparatively high diffusivity of oxygen in decomposed Y-336 sounds for the minor importance of strains locked on grain boundaries during the nucleation of Y-123 phase by heating from 880 °C to 940 °C and formation of loosely connected grains in the matrix of insulating phase Y_2BaCuO_5 . This implies a qualitatively different situation from that in mixed phase $Y_{1.2}Ba_{0.8}CuO_4$ where Y-123 phase is formed by the solid state reaction in solid solution of starting oxides.

Since the elastic contribution G_{el} to Gibbs free energy G is of minor importance in formation of new nuclei with radius r the interfacial energy $E_i = 4 \pi r^2 \cdot \gamma$ is balanced by the volume energy introduced by O-O repulsion energy $E_r = 4 \pi r^3 E_0/3$ ($E_0 \sim 0.16$ eV) with corresponding reduction of term $\tau \sim \exp(G/kT)$. A rather rough estimation for the grain radius $r = 3 \gamma/E_r$ gives for $\gamma \sim 1$ J/m² [12] $r \sim 2$ μ , in good agreement with the result of the microscopic observation of decomposed Y-336.

The picture of loosely connected grains in Y-336 is contrasted by the measurements of AC susceptibility.

Whereas susceptibility in ceramic samples exhibits two steps [13, 14] (Fig. 4) associated with the properties of grains and intergranular links [15] the transition in Y-336 reveals a rather narrow single step ($\Delta T_c \sim 2.7$ K) followed with a tail protruded to lower temperatures. Furthermore, in ceramic samples these steps are shifted apart on increasing the amplitude of the applied magnetic field in the explored range ($0.02 < H_0 < 1$ Oe). Therefore, this step may be associated with the properties of $YBa_2Cu_3O_{7-\delta}$ grains in accordance with above discussion and with previous findings [15]. We note however that the transition in Y-336 is also qualitatively different from those observed in powdered $YBa_2Cu_3O_{7-\delta}$ samples, where the transition, although rather insensitive to H_0 [15], is usually broad ($\Delta T_c < 10$ K) and continues smoothly into tail. This probably arises from a wide distribution in the size, shape, orientation and possibly quality of the individual grains. Therefore, rather narrow diamagnetic transition observed for sample Y-336 indicates much narrower distribution of the above parameters. The same conclusion is also reached from the imaginary part (χ_{im}) of the AC susceptibility (associated with loss) also shown in the figure 3. Whereas in powdered samples only a small bump in the broad loss distribution appears [3] a rather narrow maximum centered at around 0.5 χ_{im} is observed for sample Y-336. Therefore, the distribution of the grain sizes in Y-336 is narrower and/or the average grain size larger (larger χ_{im} at maximum in respect χ_{re} at low temperature ($\chi_{im}/\chi_{re} \sim 0.05$)) than that in usual Y-123 ceramic samples. As

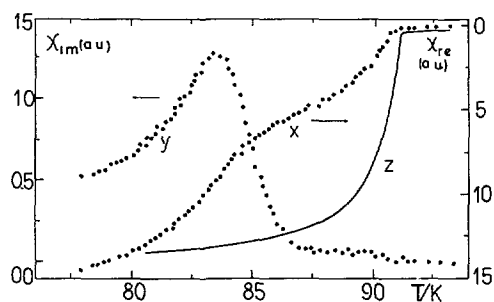


Fig. 4. — Diamagnetic transition to SC state of Y-123 : sample a ($p = 0.8$ GPa) decomposed in real part X and imaginary part Y. The continuous line Z is diamagnetic transition in Y-336 plotted in figure 3.

evidenced from the absence of the second peak in χ_{im} and of corresponding second step in χ_{re} the intergrain coupling is either far too weak or this coupling does not influence the SC properties in Y-336. The existence of very weak intergrain coupling is however inferred from the slow increase of χ_{re} and nonzero χ_{im} at lower temperatures.

In conclusion, the resistive response of the samples Y-Ba-Cu-O to the step like increase of the oxygen pressure gives an useful insight in elastic properties on grain and twin boundaries. The SC transition widths are in close correlation with these elastic properties.

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