

## **MICROBALANCE AND RELATED STUDIES OF HIGH-TEMPERATURE SUPERCONDUCTORS**

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### **Abstract**

Many properties of oxide superconductors depend on the oxygen concentration and its distribution in the samples. The microgravimetric method is very useful to study of oxide superconductors, as it allows investigations in vacuum and controlled environments in classical applications: thermogravimetric analysis for the study of solid-state reactions, determinations of oxygen contents in redox reactions and the combined measurement of mass and additional parameters, e.g. evolved gas analysis etc. Single-phase samples of high-temperature superconductors were synthesized from stoichiometric mixtures of high-purity oxides and carbonates. Appropriate amounts of the precursor powders were homogenized manually or by a mechanical ball mill and subsequently calcined at temperatures in the 800 to 950°C range with intermediate grinding to ensure homogenous reaction. The lattice parameters of all preparations were controlled, in both initial and final experiments, by the X-ray powder method (CuK $\alpha$  radiation), using a Stadi P (Stoe) diffractometer with a position-sensitive detector. It is well known that temperature and mass can be measured with an accuracy higher by orders of magnitude than it is still possible for the thermoanalyst to determine the transformation temperatures or the mass changes due to overlapping partial reactions. Applications of Cahn microbalance to study of high-temperature superconductors are presented.

**Keywords:** controlled environment, high- $T_c$  superconductors, kinetics, microgravimetric investigations

### **Introduction**

The oxygen stoichiometry in high- $T_c$  superconductors [1] is a crucial physical-chemical problem because all these compounds are oxides and, moreover, because the superconducting properties are closely related to the mixed-valency states contained in these compounds, mixed-valency states which are controlled by the oxygen stoichiometry [2–4]. Moreover, oxygen vacancies  $x$  may act as pinning centers influencing the pinning force [5, 6]. Thus, a systematic study of  $T_c$  and  $F_p$  as a function of  $x$  is of great interest. The high- $T_c$  superconductors have very short coherence lengths ( $\sim 4\text{--}30$  Å) and hence only very-fine, atomic-scale defects or perturbations are like to be efficient pinning sites. The desired flux pinning enhancement in high- $T_c$  superconductors may, in principle, be achieved by two entirely different approaches; by

a processing route and by a chemical substitution route. Various processing techniques such as neutron/proton irradiation, precipitation reaction, and shock-wave loading have proved effective, in creating defects for pinning enhancement. In chemical substitution route the superconductor lattice may be locally disturbed at the unit-cell or subunit-cell level to create coherence-length-scale defects. The chemical route is inherently more desirable because it is less likely to interfere with various required processing steps such as sintering, texturing, and wire fabrication. The microgravimetric method is very useful in analysis of oxide superconductors, because it enables investigations in vacuum and controlled environments [7–35] in classical applications: thermogravimetric analysis for the study of solid state reactions [9, 11, 13, 21], kinetic and thermodynamics of reaction [28, 31, 32], determination of oxygen content in redox reactions [8, 10, 12, 14–16, 19–23, 25–30, 33], as well as in combined measurement mass and additional parameters, for example evolved gas analysis etc. [7]. Dynamic vacuum protects from readsorption of oxygen from environment [7, 31, 32]. Hydrogen has an extremely simple electronic structure and a small mass but is nevertheless capable of causing substantial perturbations of local electron density with a comparatively slight distortion of the lattice. The introduction of hydrogen into a superconducting oxide might therefore provide important information about properties of the material [17, 18, 24, 29].

Investigations of the influence of the oxygen isotope substitution on the properties of the high- $T_c$  oxide superconductors [28] is very important in understanding the mechanism of superconductivity [36]. The observation of an oxygen isotope effect provides supporting evidence that phonons play a role in the electron pairing mechanism [37]. It is well known that temperature and mass can be measured with an accuracy higher by orders of magnitude than it is still possible for the thermoanalyst to determine the transformation temperatures or the mass changes due to overlapping partial reactions. In this paper applications of Cahn ultra-microbalance to study of high-temperature superconductors are presented.

## Experimental

All the samples of '123' and '214' superconductors were prepared by direct solid state reaction using oxides of at least 99.99% purity. The first and second calcinations were carried out at 930 and 970°C for 24 h, each with intermittent grinding at 600°C for 4 h in an oxygen flow. The powder samples were then ground and pressed into pellets. Rectangular pellets of size suitable for resistivity measurements were made and sintered in oxygen flow at 980°C for 20 h and then furnace cooled to room temperature. The oxygen contents were measured by iodometric titration with reproducibility of at least 0.02. The DC four probe resistivity measurements were performed on the pellets to which copper contacts were attached using silver paint. The in situ measurements of the oxygen loss were performed in a Cahn RG ultramicrobalance system permitting to follow the decomposition in a dynamic vacuum of  $\approx 10^{-6}$  torr. The samples were heated up to temperature of the experiment with a constant rate of  $10^\circ\text{C min}^{-1}$ . Some samples of '214' were annealed under dynamic vacuum (DV) at temperatures up to 1000°C for periods between

20–40 h with subsequent furnace cooling to room temperature. The initial mass of the samples of '123' was ca 80 mg and the drop of mass caused by the loss one oxygen atom per chemical formula  $[(RE)Ba_2Cu_3O_7 \rightarrow (RE)Ba_2Cu_3O_6 + \frac{1}{2}O_2\uparrow]$  corresponded to  $\approx 2$  mg. In order to determinate disturbances which affect the accuracy of weighing in vacuum or in controlled atmosphere [38–41], blank runs were used to correct the data obtained during kinetic runs.

Apparent mass changes did not exceed  $\pm 20$   $\mu\text{g}$ . As the accuracy of the measurements was better than  $\pm 20$   $\mu\text{g}$  estimation of the content in the sample was at the level of at least  $\pm 0.01$  per chemical formula. Loose powder  $(RE)Ba_2Cu_3O_7$  samples were placed in a small quartz crucible in vicinity of a NiCr–Ni thermocouple. The system was first evacuated down to  $10^{-7}$  torr and the sample was annealed at  $120^\circ\text{C}$  during 20 h to remove adsorbed gases and moisture. After that samples were heated up to temperature of measurement with a constant rate of  $10^\circ\text{C min}^{-1}$ .

To assure the same distribution of the grain size small samples used in measurements were for given RE always taken from a larger portion of an original  $(RE)Ba_2Cu_3O_7$  preparation. In most instances the measurement duration was long enough (sometimes up to 200 h) to approach equilibrium. Interaction of hydrogen with  $La_2CuO_4$ ,  $La_{1.8}Sr_{0.2}CuO_4$  and  $Sm_{1.85}Ce_{0.15}CuO_4$  was studied in the same apparatus. Pure gaseous hydrogen, produced through the decomposition of the hydride of Ti, was then admitted into the evacuated balance chamber. The hydrogen pressure was 600 torr. After that samples were heated up to temperature of the experiment at low heating rate of  $30^\circ\text{C h}^{-1}$ .

NMR measurements were performed using the pulse SHR-100 spectrometer at 60 MHz. The lattice parameters of all preparations were controlled, in both initial and final experiments, by the X-ray powder method ( $CuK_\alpha$  radiation) using Stadi P (Stoe) diffractometer with position sensitive detector.

## Results and discussion

The influence of the ionic radius of RE element on the bonding of the oxygen atoms in the Cu(2)–O planes of '123' compounds was investigated [35].

The oxygen loss measurements were performed for different  $(RE)Ba_2Cu_3O_6$ , ( $RE=Y, Er, Nd$ ) preparations (in the initial state  $x_i=0$ ) isothermally heated in the range of  $700\text{--}850^\circ\text{C}$ . The decomposition of the samples was started after isothermal temperature was reached. Pertinent oxygen loss curves are exemplified in Fig. 1 for  $Y_1Ba_2Cu_3O_6$  preparation. Prior to further analysis, the oxygen loss data ( $x_i$  values) were normalized. In this case desorbing oxygen is associated with total decomposition of tetragonal structure of compounds into non-identify products, where in the final stage cooper is monovalent. Final oxygen content always should be equal 5, independently of thermal decomposition.

The decomposition reaction of the type



carried out at constant temperature should follow a simple exponential relation (first order process) if all grains of the preparation are of the same size. The bonding of the oxygen atoms was investigated by gas evolution measurements and interpreted with a first order desorption model for the evolution process [42]. The samples consisted of grains of different size, decomposing with different rates, it was anticipated that the overall oxygen loss may be described by the sum of appropriate number of exponential terms depending on the grain size distribution. It has been found that for our powdered samples the number of such exponents can be limited to two terms corresponding to quick and slow decomposition rates in which small and large grains are involved:

$$(1-x_t) = A \exp(-k_1 t) + B \exp(-k_2 t)$$

where  $x_t$  is the value reached after time  $t$ , and  $k_1, k_2$  are the rate constants.

The solid lines in Fig. 1 were calculated using the above equation and appropriate constants. It should be emphasized that the agreement between calculated and experimental results is quite good. Utilizing the Arrhenius relation it was plotted  $\log k(k_1 \text{ or } k_2)$  vs. reciprocal temperature (Fig. 2). The activation energies estimated for  $(RE)Ba_2Cu_3O_6$  ( $RE=Er, Y, Nd$ ) compounds were 3.2; 3.0 and 2.7 eV, respectively. The activation energies of oxygen loss are reciprocal function of  $(RE)^{3+}$  ionic radius [42] in these cuprates.

Studies of oxygen content and ordering in the different '1 2 3' phases show that as the RE ion size increases the rate of fall in  $T_c$  with oxygen content increases [43–45] and the plateaux width become narrower.

In air, the orthorhombic to tetragonal phase transition temperature decreases rapidly with increasing RE size from  $\approx 750^\circ\text{C}$  for Er to  $\approx 550^\circ\text{C}$  for Nd [46]. The implications are that tetragonal REBCO exists over much wider temperature region for large RE's e.g. in air, tetragonal YBCO exists over a temperature range of  $\approx 1003^\circ\text{C} - 650^\circ\text{C} = 353^\circ\text{C}$ ,

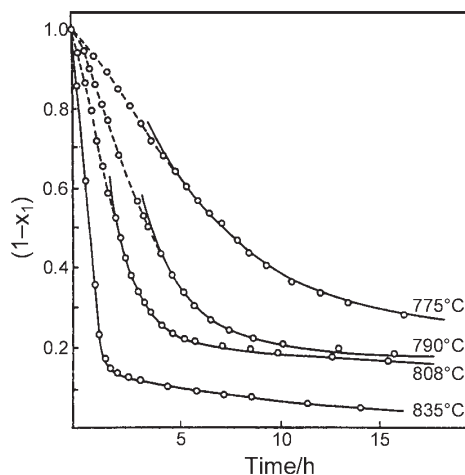


Fig. 1 Plot of  $(1-x_t)$  vs. time for yttrium preparation

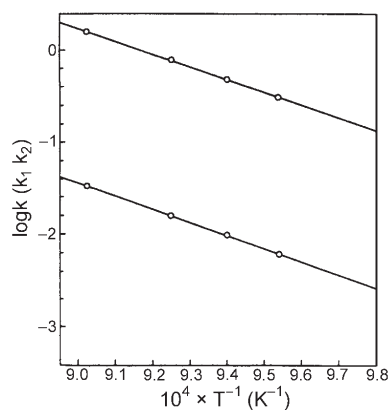


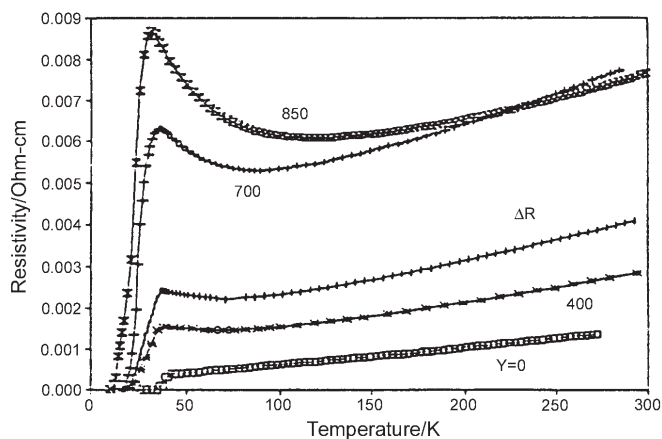
Fig. 2 Arrhenius plots for yttrium preparation

whereas the corresponding polymorph of NdBCO exists over the temperature range  $1142^{\circ}\text{C}-550^{\circ}\text{C}=592^{\circ}\text{C}$ . In effect the REBCO's of larger RE size have a higher entropy and oxygen is more disordered than for the smaller RE's. Consequently, the low temperature ordered superstructures are predicted to form at lower temperatures and higher oxygen contents for the larger RE's. Experimental evidence for this comes from the thermodynamic studies of NdBaCuO [47].

The existence of two plateaux at 90 and 60 K in  $T_c$  vs. oxygen stoichiometry plots is related to the existence of the different oxygen superstructure regions. A phase separation model has been put forward to explain the effect [48–55]. Evidence for phase separation near  $7-x=7.0$  has been demonstrated by Claus *et al.* [53] in the structural and electrical characterisation studies of single crystals. The same crystal was found to have two distinct 'c' parameters and the resistivity and magnetic susceptibility were found to be broadened at  $T_c$ . In another study on single crystals, the 'c' parameter was found to increase beyond optimal doping and a distinct double transition was observed in susceptibility data [55].

The use of doping to modify the defect structure and properties in REBCO is growing in importance in relation to both device manufacture (e.g. for barrier layers and contacts) and bulk processing (e.g. for seeding and joining). For doping on all the possible cation sites in REBCO there is known to be a strong influence on the oxygen content, ordering and mobility. Future progress in applications of doped REBCO materials will stand to gain from detailed studies of the influence of chemistry on oxygen thermodynamics and kinetics.

The resistivity measurements performed on the '214' phases show a systematic change in the transition temperature and normal state resistivity as shown in Fig. 3. The transition temperature  $T_c$  decreases with increasing annealing temperature under dynamic vacuum. The normal state resistivity changes from metallic to semiconducting-like at low-temperatures. The room-temperature resistivity increases and the  $T_c$  decreases with increasing oxygen vacancies. The sample annealed at  $1000^{\circ}\text{C}$  was not



**Fig. 3** Temperature dependence of resistivity for various samples of  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_{4-y}$ . The annealing temperatures are shown

characterised in terms of its resistivity since it had decomposed into  $\text{La}_2\text{O}_3$  and other phases and the pellet disintegrated after 24 h.

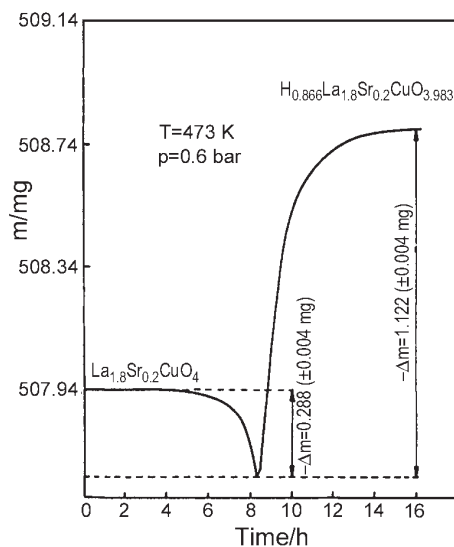
**Table 1** Lattice constants and unit-cell volume of  $\text{H}_x\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_{4-y}$

$\text{H}_x\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_{4-y}$	Oxygen content	Hydrogen content, $x$	Lattice constants/ $\text{\AA}$		Cell volume/ $\text{\AA}^3$
			$a$	$c$	
$\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_{4-y}$	4.00	0.00	3.774	13.232	188.43
400°C DV	3.98	0.00	3.774	13.229	188.42
900°C DV	3.97	0.00	3.774	13.224	188.35
950°C DV	3.96	0.00	3.774	13.224	188.35
$\text{H}_{0.02}\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_{3.99}$	3.99	0.02	3.776	13.237	188.74
$\text{H}_{0.1}\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_{3.98}$	3.98	0.10	3.774	13.267	188.94
$\text{H}_{0.3}\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_{3.99}$	3.99	0.30	3.774	13.322	189.72

The results of the iodometric titration measurements are also given in Table 1. These correlate well with the resistivity results. It is surprising that this system loses only one percent oxygen even if it is annealed in dynamic vacuum at 950°C which is equivalent to the calcination temperature of the compound. In present case it was observed almost a negligible change in the  $a$  and  $c$  parameters with increasing oxygen vacancies (Table 1). Formation of 1% oxygen vacancies does not produce much change in the lattice parameters.

Influence of hydrogen on the magnetic and superconducting properties of  $\text{La}_2\text{CuO}_4$ ,  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  systems has been studied. It has been established that the interaction of hydrogen with the insulating  $\text{La}_2\text{CuO}_4$  samples results in reduction of oxygen [14, 16, 18, 29] while the reaction of  $\text{H}_2$  with  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  can be interpreted as a several parallel and follow-up reactions as is shown in Fig. 4. The mass loss corre-

sponds to an oxygen loss (reduction from cuprate to  $\text{Cu}_2\text{O}$ ), a mass gain to the solution of hydrogen. The mass however can also increase, if the water vapour, which is formed by the reduction of the oxygen content does not evaporate but reacts with  $\text{La}_2\text{O}_3$  to hydroxide  $\text{La}(\text{OH})_3$  [29]. The hydroxide decompose as the temperature is further increased. The final step occurs at the formation of metallic copper  $\text{Cu}^0$  at equilibrium conditions.



**Fig. 4** Gravimetric kinetic curve for the process of interaction of hydrogen with  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$

Studies of the hydrogenated samples by X-ray structural analysis showed that the reflections characteristic of the tetragonal structure of the original sample persist, but their intensity decreased with increasing hydrogen concentration, and the noise increases. This ‘amorphization’ of the X-ray diffraction patterns apparently results from the grinding of the samples, to dimensions smaller than a certain critical dimension in the region  $\leq 0.1 \mu\text{m}$ .

No secondary phases were present in the diffraction patterns. In addition, an analysis of the X-ray diffraction patterns showed that the lattice constant along the tetragonal axis increases systematically with increasing hydrogen concentration (Table 1). In this manner were produced samples of  $\text{H}_x\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_{4-y}$  with  $x=0, 0.02, 0.1, 0.3,$  and  $0.866$ . To determine the superconducting transition temperature, it has been measured the *rf* magnetic susceptibility. In samples with  $x \geq 0.1$ , the superconductivity was suppressed essentially completely. In the sample with  $x=0.02$ , on the other hand (Fig. 5), the transition onset temperature  $T_c$ , corresponding to the slope change in  $\chi$ , remained the same as that of the original sample. The amount of superconducting phase, however, decreased by a factor of 1.5. The absorption of hydrogen thus results in a decrease in the amount of superconducting phase in the cuprate. In

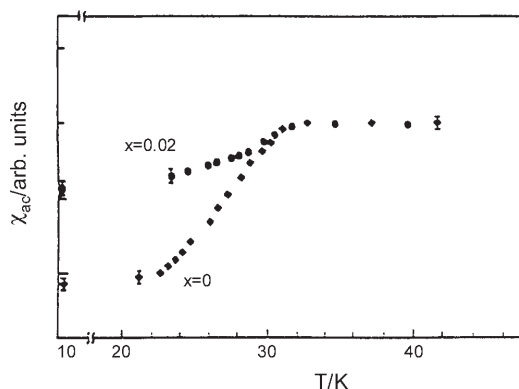


Fig. 5 Temperature dependence of the magnetic susceptibility of  $H_xLa_{1.8}Sr_{0.2}CuO_{4-y}$

other words, the superconductivity is suppressed in certain parts of the cuprate (phase separation). The hydrogen concentration in the sample with  $x = 0.1$ , at which the superconductivity is suppressed, is approximately equal to the concentration of the Sr dopant atoms in this ceramic. At this concentration, the mechanism for the suppression of the superconductivity by hydrogen in the lanthanum-strontium ceramic is probably associated with a neutralization of holes as hydrogen localizes in a copper-oxygen plane. That hydrogen can localize in this plane, in the positions with the coordinates  $(\frac{1}{2}, \frac{1}{2}, 0)$  and  $(0, 0, \frac{1}{2})$ , is confirmed by an analysis of the sizes of the interstices based on crystallographic data and the ionic radii of the elements. These positions are equivalent, and each has four  $O^{2-}$  ions (with an ionic radius of  $1.40 \text{ \AA}$ ) in its neighborhood. These oxygen ions form interstices with the size of about  $1 \text{ \AA}$  – the optimum size for being filled by hydrogen atom. Along the tetragonal axis, these positions lie between two  $La^{3+}$  cations, whose interaction with the hydrogen cation (proton) is apparently the reason for the increase in the lattice constant  $c$  (Fig. 6).

NMR measurements at a frequency of 60 MHz for a sample with  $x=0.866$ , showed that the proton-resonance signal is a single symmetric line of Gaussian shape

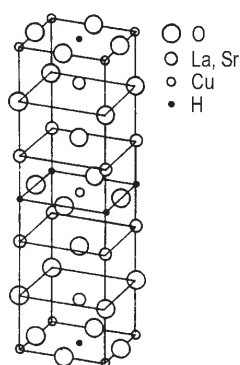


Fig. 6 Localization of hydrogen atoms in the unit cell of  $La_{1.8}Sr_{0.2}CuO_4$



with a width of 63 kHz, which is essentially independent of the temperature. It has been estimated the width of the NMR line caused by the dipole interaction of proton with nearest La and Cu nuclei and protons, with oxygen occupying the positions under consideration.

From appropriate formulas [17] it has been estimated the linewidth to be  $\approx 30$  kHz, or comparable to the width found experimentally. Finally, there is yet another circumstance: If hydrogen does occupy these positions, the composition of the resulting samples will be  $H_{1.0}La_{1.8}Sr_{0.2}CuO_4$ . This composition is close to the composition with the maximum hydrogen content found in experiments, from the saturation of the lanthanum-strontium ceramic with hydrogen. It follows from results that hydrogen occupies position in the center of the Cu–O planes of the unit cell. This position is in a region of a distribution of the electron density of oxygen. The obtained results indicate that the quantum chemistry calculations are extremely necessary for mechanism and theory of high- $T_c$  superconductivity.

## Conclusions

The results obtained indicate that phase separation in high- $T_c$  superconductors is connected with heterogeneous distribution of charges in Cu(2)–O planes. For systematic progress, basic research into the thermodynamics and materials chemistry should proceed in parallel with processing studies. More experiments on well-characterized samples are required, and quantum chemistry calculations are extremely necessary, because the role of geometric and electronic factors in these compounds is still unclear. Such calculations can be fundamental for theory and mechanism of high- $T_c$  superconductivity. Further basic knowledge of the high temperature chemistry of cuprates for a wide range of rare earths, and with appropriate dopant additions is necessary for successful application of these materials in bulk and thin film form.

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