

OXYGEN NON-STOICHIOMETRY AND DIFFUSION IN $\text{RBa}_2\text{Cu}_3\text{O}_{6+x}$ ($R=\text{Y, Gd, Ho}$) INVESTIGATED BY TG METHOD

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Abstract

By means of thermogravimetry (TG) and chemical analysis equilibrium dependencies of oxygen content in $\text{GdBa}_2\text{Cu}_3\text{O}_{6+x}$ and $\text{HoBa}_2\text{Cu}_3\text{O}_{6+x}$ on temperature and P_{O_2} were studied. It is found that at equal temperature and P_{O_2} the oxygen content in $\text{RBa}_2\text{Cu}_3\text{O}_{6+x}$ increased in order Ho-Y-Gd.

On the basis of Fick 2nd law mathematical procedures to determine diffusion coefficients of oxygen from TG data were developed. The oxygen diffusion coefficients in $\text{RBa}_2\text{Cu}_3\text{O}_{6+x}$ ($R=\text{Y, Gd, Ho}$) were evaluated in a wide temperature (300–900°C) range (at $P_{\text{O}_2}=0.21$ bar). The developed model rather satisfactory describes oxygen diffusion processes in phases under investigation. It is found that for all studied compounds oxygen diffusion in orthorhombic phase happened faster than in tetragonal one. The values of diffusion coefficients increase in order Ho-Y-Gd with increasing of ionic radius of the rare earth element.

Keywords: $\text{GdBa}_2\text{Cu}_3\text{O}_{6+x}$, $\text{HoBa}_2\text{Cu}_3\text{O}_{6+x}$, oxygen non-stoichiometry, oxygen diffusion, $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$

Introduction

The superconductivity properties of phases $\text{LnBa}_2\text{Cu}_3\text{O}_{6+x}$ are well known to depend on their oxygen non-stoichiometry (x). Therefore the investigation of oxygen exchange between the gaseous phase and the solid state material is of great importance. For this purpose it is necessary to establish the equilibrium P - T - x diagrams represented the relationships between oxygen non-stoichiometry of these compounds, temperature and oxygen partial pressure (P_{O_2}). The another task to be solved is the evaluation of oxygen diffusion coefficients that determine the kinetics of the oxidation and reduction of phases under the consideration.

Nowadays the P - T - x diagrams are well studied for some $\text{RBa}_2\text{Cu}_3\text{O}_{6+x}$ phases only [1–3]. The most of available information concerning the parameters of oxygen diffusion (effective activation energy E and pre-exponential factor D_0) is referred to $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ (Y123) phase. The oxygen diffusion coefficients (D) have been determined by means of different techniques including thermogravimetry (TG) [4–6], volumetry [7], measurements of resistance [8–10] and dc polarization [11]. The literature data [4–15] for oxygen diffusion parameters are presented in Fig. 1 as a

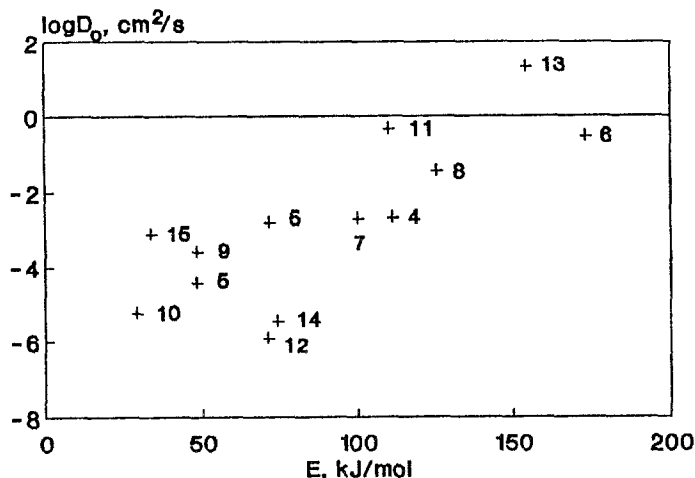


Fig. 1 The literature data concerning effective activation energy E and pre-exponential factor D_0 of oxygen diffusion in Y123 phase (numbers of points correspond to numbers of references)

function $\log D_0 = f(E)$. The values 4–14 were obtained by authors of works [4–14] respectively. The values 15 are calculated by authors of this article from data [15] using least-squares fitting. As can be seen there are significant disagreements in obtained results. For another $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_{6+x}$ phases the analogous data are extremely limited in number.

In this article we present the results of the investigation of equilibrium dependencies $x = f(T, P_{\text{O}_2})$ for $\text{Gd}\text{Ba}_2\text{Cu}_3\text{O}_{6+x}$ (Gd123) and $\text{Ho}\text{Ba}_2\text{Cu}_3\text{O}_{6+x}$ (Ho123) phases, determination of oxygen diffusion coefficients in $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_{6+x}$ ($R = \text{Y, Gd, Ho}$), and the application of a mathematical model for simulation of process of oxygen diffusion.

Experimental

Synthesis

The synthesis of single phase $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_{6+x}$ ($R = \text{Y, Gd, Ho}$) samples was performed by means of freeze and spray drying techniques using $\text{R}(\text{NO}_3)_3$ ($R = \text{Y, Gd, Ho}$), $\text{Ba}(\text{NO}_2)_2$, and $\text{Cu}(\text{NO}_3)_2$ solutions. The decomposed (850°C, 30 min) salt powders were annealed at 920–950°C during 12 h. After annealing all samples were slowly cooled with furnace. To obtain samples with fixed oxygen content the additional annealings at different temperatures with following quenchings were applied.

Analysis

To control phase composition of samples the powder X-ray diffraction analysis (radiation CuK_α) was used. TG data were obtained on thermobalance "Sartorius 4433" (Germany) in temperature interval 300–900°C under different oxygen

partial pressures (in the gas flow). For studying of equilibrium dependencies $x=f(T, P_{O_2})$ the TG with small rate (1–2 K min⁻¹) of heating and cooling was carried out. Before heating all samples were exposed at 300°C in order to remove adsorbed admixtures of CO₂ and H₂O and to reach the equilibrium between a sample and gaseous phase. The curves $\Delta m=f(T)$ were converted into dependencies $x=f(T)$ according to the equation:

$$x = x_0 + \frac{\Delta m M r_0}{m_0 A} \quad (1)$$

where Δm – the change of mass, x_0 and m_0 – initial values of oxygen non-stoichiometry and mass of sample respectively, $M r_0$ – relative molecular mass corresponding to the composition $R B a_2 C u_3 O_{6+x}$ ($R=Y, Gd, Ho$), $A=16$ g mol⁻¹ atomic weight of oxygen. To determine initial values of oxygen non-stoichiometry in these experiments the iodometric titration was used. The average particle sizes of powders were measured by means of dynamic light scattering analysis ("Analysette 22", Germany).

Mathematical model

The mathematical procedures to evaluate the values of oxygen diffusion coefficients were developed on the basis of Fick 2nd law. The average oxygen concentration (c) for spherical particle (with radius a) can be presented by the following equation [16]:

$$\frac{c - c_k}{c_0 - c_k} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D \tau}{a^2}\right) \quad (2)$$

where c_0 – the initial oxygen concentration, c_k – the final equilibrium oxygen concentration, τ – duration of isothermal annealing, $D=D_0 \exp(-E/RT)$ – diffusion coefficient of oxygen. With accuracy of 1% one could be limited by 16 terms in Eq. (2). The polythermal annealing with constant rate V could be presented as a sequence of quasi isothermal annealings with duration equal to $\Delta T/V$, where ΔT is a step of temperature (5–7 K). The left part of Eq. (2) was replaced by the equivalent expression

$$\frac{c - c_k}{c_0 - c_k} = \frac{x - x_k}{x_0 - x_k} \quad (3)$$

where x_i is the corresponding value of oxygen non-stoichiometry. In doing so the value x for each quasi isothermal annealing was the value x_0 for next one. The calculation of diffusion coefficients of oxygen was carried out by the method of iteration using a specially developed program, the error of calculation being no greater than 10%.

The well known experimental dependencies for equilibrium values of oxygen non-stoichiometry x_k of Y123 phase vs. temperature at different P_{O_2} [1, 2] were also used in this model. In case of Gd123 and Ho123 phases we used our own data described below.

From obtained dependencies $\log D=f(1/T)$ the parameters of oxygen diffusion (E and D_0) were calculated using least-squares fitting. To choose more reliable values the statistical analysis (comparison of dispersion of reproduction and dispersion of adequacy) was carried out.

The developed computer model could be successfully applied for simulation of processes of oxidation and reduction of compounds under the investigation. The model based on obtained values of D allows to calculate the change of oxygen non-stoichiometry of samples for any regime of thermal treatment (heating, cooling, isothermal annealing, mixed regimes). For description of behavior of powders and low density pellets the Eq. (2) is applied. For high density ceramics and single crystals the mathematical model in approximation of plate (with thickness h) can be used. In this case Eq. (2) is substituted by the following one [16]:

$$\frac{c - c_k}{c_0 - c_k} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 \pi^2 D \tau}{h^2}\right) \quad (4)$$

where all symbols are the same as in Eq. (2). The diffusion in powders and untextured bulk materials could be considered in an approximation of isotropic medium, that could be justified by random distribution of grains in samples. For textured ceramics and single crystals the anisotropy of oxygen diffusion would be taken into account [17].

So, basic assumptions of the calculation procedures are:

- 1) at small change of oxygen non-stoichiometry ($\Delta x \leq 0.05$) parameters of oxygen diffusion do not depend on oxygen content;
- 2) if the polythermal annealing is presented as a sequence of quasi isothermal ones, the temperature of each isothermal step is taken to be constant and equal to average value;
- 3) at transfer from one quasi isothermal step to another the initial oxygen content is assumed to be the same for whole grain volume.

Results and discussion

Oxygen non-stoichiometry

The equilibrium dependencies $x=f(T)$ of Gd123 and Ho123 samples were obtained at different P_{O_2} values in range 0.01–1 bar. By way of example, the results for $P_{O_2}=0.21$ bar are given on Fig. 2. It should be noted that presented data were averaged over three parallel experiments (cycles of heating and cooling). The literature data for Y123 phase [2] are also presented. As one can see the oxygen content in all investigated compounds changes in the same manner, but absolute values of x

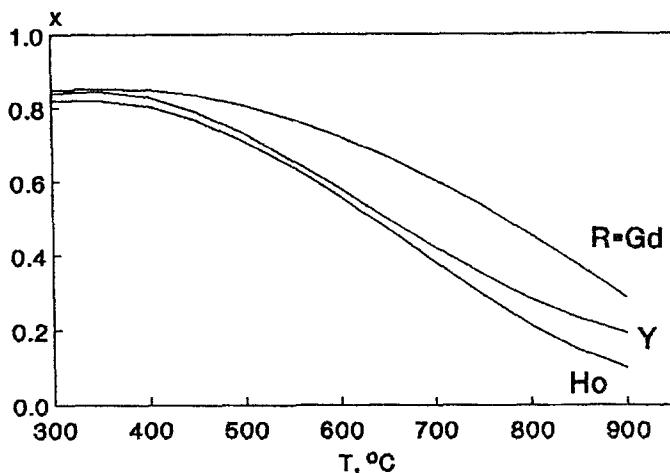


Fig. 2 Equilibrium dependencies $x=f(T)$ for Y123 (from [2]), Gd123 and Ho123 compounds ($P_{O_2}=0.21$ bar)

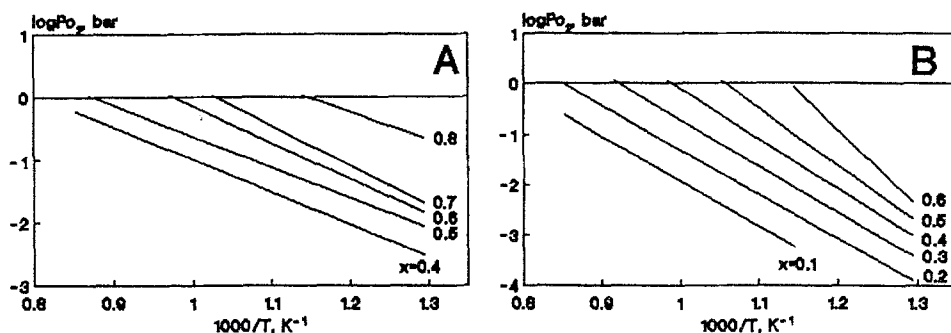


Fig. 3 The fragments of equilibrium P - T - x diagrams for Gd123 (A) and Ho123 (B) compounds

(at equal temperature) increase in order Ho–Y–Gd with increasing of ionic radius of the rare earth element.

On the basis of experimental results the fragments of P - T - x diagrams for Gd123 and Ho123 phases have been constructed (Fig. 3). The coefficients of linear dependencies $\log P_{O_2}=A+B/T$ as well as errors of their determination are presented in Tables 1–2.

Using the data of Tables 1–2 the partial molar enthalpy of oxygen solution (ΔH_{O_2}) in Gd123 and Ho123 compounds was calculated at different values of x . As one can see from Table 3 our data related to Gd123 phase are greater than results of Hasegawa *et al.* [3], that could be caused by differences in determined initial values of oxygen content in Gd123 samples. However, the character of change of ΔH_{O_2} with increasing of oxygen non-stoichiometry (within range $0.4 \leq x \leq 0.65$) is the same in both cases.

Table 1 Coefficients (and errors of their determination) of equilibrium dependencies $\log P_{O_2} = A + B/T$ ($x = \text{const}$) for Gd123 phase

x	A	S_A	B	S_B
0.40	4.18	0.23	-5.18	0.82
0.45	4.14	0.35	-4.93	1.26
0.50	4.23	0.40	-4.85	1.41
0.55	4.68	0.44	-5.11	1.64
0.60	5.53	0.50	-5.69	2.15
0.65	6.52	0.60	-6.35	2.96
0.70	7.06	0.65	-6.60	3.31
0.75	6.60	0.49	-5.98	1.99
0.80	4.86	0.19	-4.25	0.59
0.85	2.87	0.09	-2.29	0.15

Table 2 Coefficients (and errors of their determination) of equilibrium dependencies $\log P_{O_2} = A + B/T$ ($x = \text{const}$) for Ho123 phase

x	A	S_A	B	S_B
0.05	7.10	0.11	-9.37	0.70
0.10	6.97	0.05	-8.90	0.31
0.15	7.11	0.05	-8.74	0.28
0.20	7.45	0.07	-8.77	0.44
0.25	7.89	0.11	-8.92	0.76
0.30	8.43	0.16	-9.15	1.02
0.35	9.04	0.19	-9.46	1.31
0.40	9.76	0.22	-9.86	1.55
0.45	10.67	0.23	-10.43	1.73
0.50	11.94	0.23	-11.30	1.86
0.55	13.88	0.23	-12.68	2.02
0.60	17.19	0.22	-15.08	2.32

While absolute values of oxygen non-stoichiometry of Ho123 phase are smaller as compared with yttrium and gadolinium analogs, we could not obtain a sufficient number of experimental data in studied range of temperature and P_{O_2} for correct determination of ΔH_{O_2} at $x > 0.6$. For the analogous reason ΔH_{O_2} values for Gd123 phase were determined at $x \geq 0.4$ only. Nevertheless, the character of dependence $\Delta H_{O_2} = f(x)$ within range $0.4 \leq x \leq 0.6$ is quite similar for both phases.

In our opinion the intermediate maximum of dependence $\Delta H_{O_2} = f(x)$ at $x \approx 0.4-0.5$ (Table 3) is due to formation of superstructural modification (ortho II) like already mentioned by Yamagushi *et al.* [18] for Y123 phase. The increasing of ΔH_{O_2} at larger

Table 3 Partial molar enthalpy of oxygen solution ($\Delta H_{O_2}/\text{kJ mol}^{-1}$) in Gd123 and Ho123 phases in dependence on oxygen non-stoichiometry

x	Gd123		Ho123
	our data	data [3]	our data
0.05			-179.4
0.10			-170.5
0.15			-167.3
0.20			-167.9
0.25		-145.6	-170.8
0.30		-172.1	-175.3
0.35		-165.5	-181.1
0.40	-99.1	-165.8	-188.8
0.45	-94.4	-166.1	-199.8
0.50	-92.9	-169.7	-216.3
0.55	-97.8	-176.9	
0.60	-108.9	-180.0	
0.65	-121.7	-174.9	
0.70	-126.4		
0.75	-114.5		
0.80	-81.3		
0.85	-43.8		

values of oxygen non-stoichiometry ($x > 0.7$) could be resulted from increase of interaction energy between neighbour oxygen sites in layers (*ab*) of crystal lattice.

Oxygen diffusion

The diffusion coefficients of oxygen were determined from TG data obtained at $P_{O_2} = 0.21$ and 1 bar on the samples with different characteristics (initial value of oxygen non-stoichiometry, average grain size, density of pellets, thickness of powder layer). For statistical analysis the whole set of obtained data (about 50 experiments) was used. In result the next values were found

$$E = 92.4 \text{ kJ mol}^{-1}, D_o = 0.023 \text{ cm}^2 \text{ s}^{-1} \text{ (Y123, air)} \quad (5a)$$

$$E = 138.3 \text{ kJ mol}^{-1}, D_o = 0.886 \text{ cm}^2 \text{ s}^{-1} \text{ (Y123, oxygen)} \quad (5b)$$

$$E = 82.0 \text{ kJ mol}^{-1}, D_o = 0.0064 \text{ cm}^2 \text{ s}^{-1} \text{ (Gd123, air)} \quad (5c)$$

$$E = 90.9 \text{ kJ mol}^{-1}, D_o = 0.94 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1} \text{ (Ho123, air)}, \quad (5d)$$

that have the most closely described the experimental data.

The results of statistical analysis for Y123 small crystalline powders and pellets are given in Table 4. As can be seen the developed model rather satisfactory describes behaviour of powders with different thickness of layer (1–8 mm), powders with different initial values of oxygen non-stoichiometry (Fig. 4), and pellets with density below 5.04 g cm^{-3} (approximately 80% from theoretical density). As for the pellets with larger density the experimental data significantly differ from the calculated ones. We consider the cause of these deviations could be the closed porosity in high density ceramics and diffusion obstacles which appear at annealing. In this case the Eq. (4) would be applied for correct description of oxygen diffusion.

Table 4 Dispersions of adequacy (σ_a) and reproduction (σ_r) and corresponding degrees of freedom (f_a, f_r) for some sets of Y123 samples studied by TG in air (heating rate is 10 K min^{-1})

Set	$\sigma_a \cdot 10^{-3}$	f_a	$\sigma_r \cdot 10^{-3}$	f_r	N^*
Powders	1.456	95	0.968	121	5
<i>$l^{**} = 1 \text{ mm}$</i>	<i>2.540***</i>	31	3.626	34	3
Powders, $l = 8 \text{ mm}$	1.887	189	1.739	208	5
Low density pellets	0.610	153	0.560	172	5
High density pellets	2223.9	122	1.348	116	4

* N is number of parallel experiments;

** l is thickness of powder layer;

*** data for $P_{\text{O}_2} = 1 \text{ bar}$ are presented by italic font.

In studies of oxygen diffusion in Y123 phase by means of coulometric titration at low P_{O_2} values we found [19], that effective activation energy of oxygen diffusion increased with increasing of oxygen partial pressure. From our point of view, this change of diffusion parameters is caused mainly influence of oxygen non-stoichiometry. To verify this, we treated our experimental data, that have been obtained by TG in air, for ranges of oxygen non-stoichiometry corresponding to orthorhombic ($0.6 \leq x \leq 0.95$) and tetragonal ($0.05 \leq x \leq 0.45$) phases separately. As can be seen from Table 5, there is a doubtless influence of oxygen non-stoichiometry on parameters of oxygen diffusion. The comparison of absolute values of D shows that for all investigated compounds oxygen diffusion in orthorhombic phase happens faster than in tetragonal one. Furthermore, the values of oxygen diffusion coefficient increase in order Ho–Y–Gd, that could be caused by change of distance and consequently interaction energy between the nearest oxygen sites in layers (ab) of crystal lattice with increasing of ionic radius of the rare earth element.

It should be noted, that obtained values of E and D_0 (5a–5d) determined for a whole variation range of oxygen non-stoichiometry are still suitable for the general description of processes of the oxidation and reduction in polythermal regime (Table 3 and Fig. 4). These values are greater than analogous ones presented in Table 5, because for their evaluation we used all experimental results including the data related to range of oxygen non-stoichiometry ($0.45 < x < 0.55$) that corresponded to ortho-

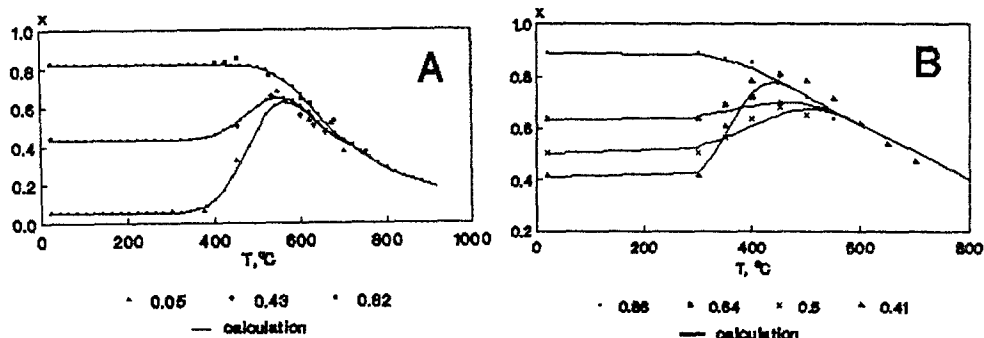


Fig. 4 The calculated curves $x=f(T)$ and experimental data for heating of Y123 (A) and Gd123 (B) powders with different initial values of oxygen non-stoichiometry

Table 5 Effective activation energies $E/\text{kJ mol}^{-1}$ and $\log D_0/\text{cm}^2 \text{s}^{-1}$ of oxygen diffusion in $\text{RBA}_2\text{Cu}_3\text{O}_{6+x}$ ($R=\text{Y, Gd, Ho}$; $P_{\text{O}_2}=0.21 \text{ bar}$)

R	Orthorhombic phase		Tetragonal phase	
	E	$\log D_0$	E	$\log D_0$
Y	73.6±12.6	-4.19±1.84	31.2±11.9	-8.10±0.74
Gd	62.6±10.3	-5.22±1.28	35.3±9.7	-6.46±1.93
Ho	59.8±5.1	-8.34±0.26	34.0±9.82	-9.96±1.08

tetra phase transition. This structural transition is accompanied by increasing of the oxygen diffusibility, that could be lead to larger values of diffusion coefficient.

Conclusion

By means of TG the oxygen non-stoichiometry of Gd123 and Ho123 compounds as a function of temperature and P_{O_2} was studied. The fragments of equilibrium $P-T-x$ diagrams for these phases were constructed. From obtained data the partial molar enthalpy of oxygen solution in Gd123 and Ho123 was calculated at different values of x .

Using TG data the diffusion coefficients of oxygen were evaluated in a wide temperature (300–900°C) range. On the basis of Fick 2nd law a mathematical model to describe the process of oxygen diffusion for different regimes of thermal treatment was developed. The model rather satisfactory describes behavior of powders and low density pellets (in approximation of the sphere particle) and high density ceramics (in approximation of the plate). The developed computer model and measurement techniques can be successfully applied for other compounds with variable oxygen content.

The separate treatment of experimental data obtained for orthorhombic and tetragonal phases respectively showed the significant change of parameters of oxygen diffusion in all investigated compounds.

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