



Comparative study of oxygen diffusion in rare earth REBa₂Cu₃O_{7-δ} single crystals (RE = Y, Er, Dy) with different impurity levels

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Abstract

We report on measurements of the chemical diffusion coefficients of rare earth cuprate single crystals REBa₂Cu₃O_{7-δ} (RE = Y, Er, Dy) grown in crucibles made of Y₂O₃-stabilized ZrO₂ and BaZrO₃. The diffusion coefficients have been determined by in situ measurement of the electrical conductivity using a four point method during the oxygenation at various oxygen partial pressures and in the temperature range of 390°C–550°C. In this range the diffusion coefficient was determined between 3.7×10^{-9} cm²/s and 6.6×10^{-8} cm²/s independent of the rare earth atom or of the different impurity levels. For all crystals we show that the in- and out-diffusion process can be described with the same time constant at each annealing temperature. Within the accuracy of $\pm 5\%$ we measure for both processes the same value for the diffusion coefficient. The temperature dependence of the diffusion coefficient obeys an Arrhenius-law for all crystals, proving that the oxygen diffusion in the rare earth RE 123 superconductors is a purely thermally activated process. The values for the activation energy show a scattering up to 30% and vary from 0.76 to 1.09 eV. There is neither a dependence of the activation energy on the central rare earth atom nor on different impurity levels. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Oxygenation of bulk samples of 123 superconductors is a major problem, both for the preparation of samples for fundamental research as well as for samples with optimised transition temperature and

pinning properties for applications. In most cases the oxygenation is done more or less according to experience rather than being based on the knowledge of the actual mechanism. The reason is that there exists little and contradicting information about diffusion coefficients of oxygen in the rare earth (RE)-123 compounds. However, the knowledge of the diffusion coefficients is important, especially due to the

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fact that in different RE-123 superconductors the annealing temperature for which the maximum transition temperature can be obtained is lowered by about 20, 100 and 200 K for the Dy, Eu and Nd systems respectively if compared with $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [1].

As shown in our earlier paper [2], in which mainly the diffusion coefficients of $\text{Gd}_{1-x}\text{Y}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals were reported, measurement of the development of the electrical conductivity $\sigma(t)$ during the oxygenation is a good method to determine the diffusion coefficients of $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals. These crystals had a diffusion coefficient of $\sim 10^{-8} \text{ cm}^2/\text{s}$.

The diffusion coefficients for different RE-123 compounds have been reported to vary by up to two orders of magnitude in respect to those of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [3]. Additionally it has been speculated that the diffusion coefficients are much higher if the residual impurity level is lower especially for the single crystals of highest purity grown in BaZrO_3 crucibles [4].

Therefore we performed a comparative study on the oxygen diffusion in crystals with different rare earth central atoms as well as with different impurity levels.

2. Experimental

2.1. Samples

The $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals were grown via a self flux method described elsewhere [5,6]. The $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and the Ca-doped $\text{Y}_{1-y}\text{Ca}_y\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals were grown in ZrO_2 -crucibles (Friatec, Mannheim). ZrO_2 -crucible material contains 7% Y_2O_3 for stabilisation and additional 3.5% Al_2O_3 as sintering aid. It is well known that the $\text{BaCuO}_2\text{--CuO}$ mixture, used as solvent for the crystal growth, reacts with the crucible material. Due to this corrosion Al, Y and Zr were solved in the melt. In the crystals Zr was not detected above the detection limit of the atomic absorption spectroscopy or micro probe analysis (0.5 at.%) and Al only to an amount of about 1% of the Cu-chain sites.

However the Y which is dissolved from the crucible substitutes the rare earth elements Er and Dy to 10–20% if crystal growth is performed in ZrO_2 -crucibles.

To avoid mixed crystals $\text{RE}_{1-x}\text{Y}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ the $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{DyBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals were grown in home made BaZrO_3 crucibles [7] using starting materials with 5N purity. For those crystals the only detected impurities were La, Sr and Zr with values between 0.0005 at.% and 0.0014 at.%. Thus the purity of these crystals is better than 99.995 at.%. The crystals chosen for the measurements had a thickness smaller than 200 μm , thus minimising the chance of flux inclusions in the crystals. The dimensions of the samples were $2\text{--}4 \cdot 0.5\text{--}1.5 \cdot 0.02\text{--}0.2 \text{ mm}^3$. The ratio of the length of the a -axes to the length of the b -axes was in all cases greater than three.

2.2. Measurements

The conductivity measurements were carried out in oxygen atmosphere (purity better than $\geq 99.995\%$) at various oxygen partial pressures ($p = 1 \text{ bar}$, 0.5 bar, 0.1 bar). The temperature ranged from room temperature up to 650°C . The conductivity was determined with four point probe measurement. Contacts were made by sputtering four platinum stripes onto the surface of the crystals (see inset Fig. 1). Gold wires were attached to the platinum pads with platinum paint. Contacts with other contacting paints were not stable over the long measurement periods. The voltage was taken from the two contacts in the middle of the crystals. To avoid any degeneration of the crystal surface by hydro-carbides originating from the platinum paint we worked with large oxygen flow rates, particularly during the stoving process of the contacting paint.

Due to the long time needed to reach the equilibrium conductivity values which correspond to the equilibrium oxygen content at a given annealing temperature we constructed a sample holder (see Fig. 1) which allows us to measure three crystals in one run at identical conditions. The sample holder was put in a quartz tube heated by a home made tube furnace. The temperature gradient in the region of the samples was less than 1 K/cm. The temperature

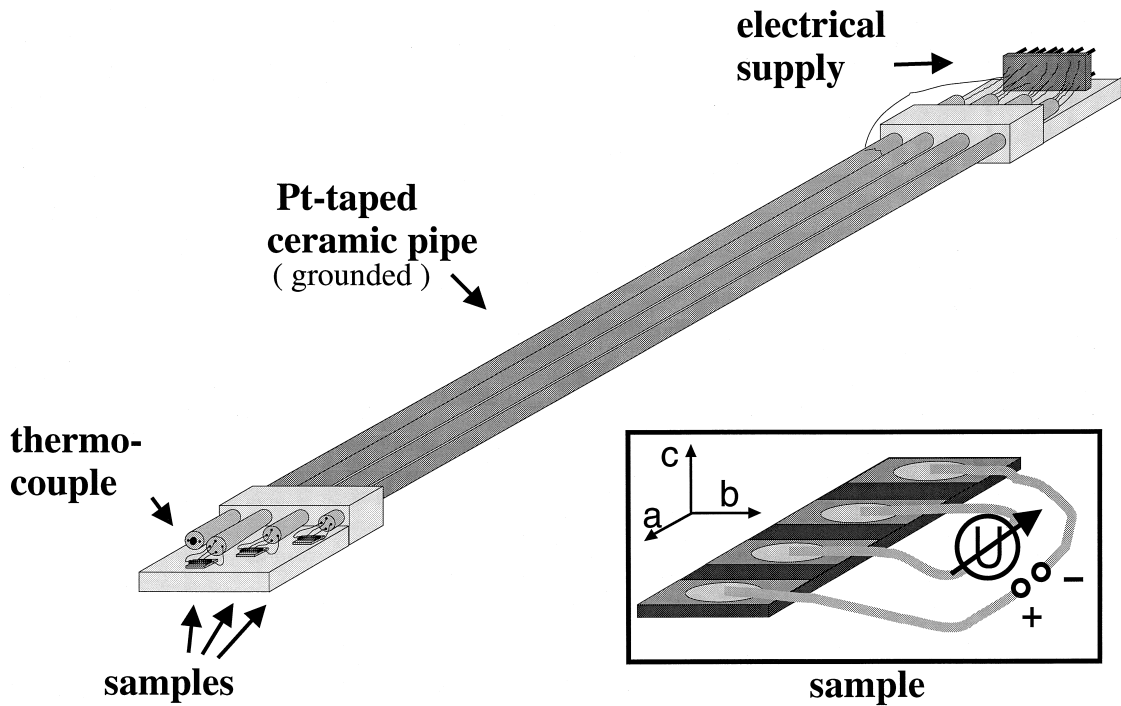


Fig. 1. Advanced sample holder with the option to measure three samples at once (inset: sample with the contacts in a four point geometry).

was determined with a Pt/PtRh10% thermocouple beside the crystals.

The voltage of the thermocouple and the bias voltage of the crystals were monitored by a HP multimeter using a selector switch to choose one of the crystals or the thermocouple. The applied current was 5 mA. With this new equipment we reach a resolution of about $\pm 0.2 \mu\text{V}$ and of about $\pm 0.5^\circ\text{C}$.

The control of the selector switch and the current supply as well as the read out of the voltage was done by a PC. The developed program allowed beside controlling and plotting of the measurements the analysis of the measured curves.

2.3. Measuring mode

The routine of the measurement consisted of the following steps (Fig. 2): the crystal was brought into equilibrium at a constant temperature T_1 . The equilibrium was reached when the value of the conductivity remained constant, indicating homogeneous oxygenation. After that a new temperature T_2 was

adjusted with a quick temperature step of 100 K/h. The conductivity first followed this fast temperature change immediately due to the ordinary temperature dependence of the conductivity. At the new temperature T_2 however the equilibrium oxygen content is different from that at T_1 , leading to diffusion so that the conductivity did slowly approach a new equilibrium value σ_c corresponding to the new oxygen equilibrium value at T_2 .

2.4. Theory

The variation of the electrical conductivity with time during the diffusion process can be described by the model diffusion in a plane sheet [8,9]. In this model the oxygen diffusion in the crystal is reduced to a one dimensional problem. The applicability of the model is justified on the one hand by the possibility to neglect the diffusion in c -direction ($D_c \sim 10^{-4} - 10^{-6} D_{ab}$ [10–12]) and on the other hand by the chosen geometry of the crystals: the crystal length l is more than three times greater than the

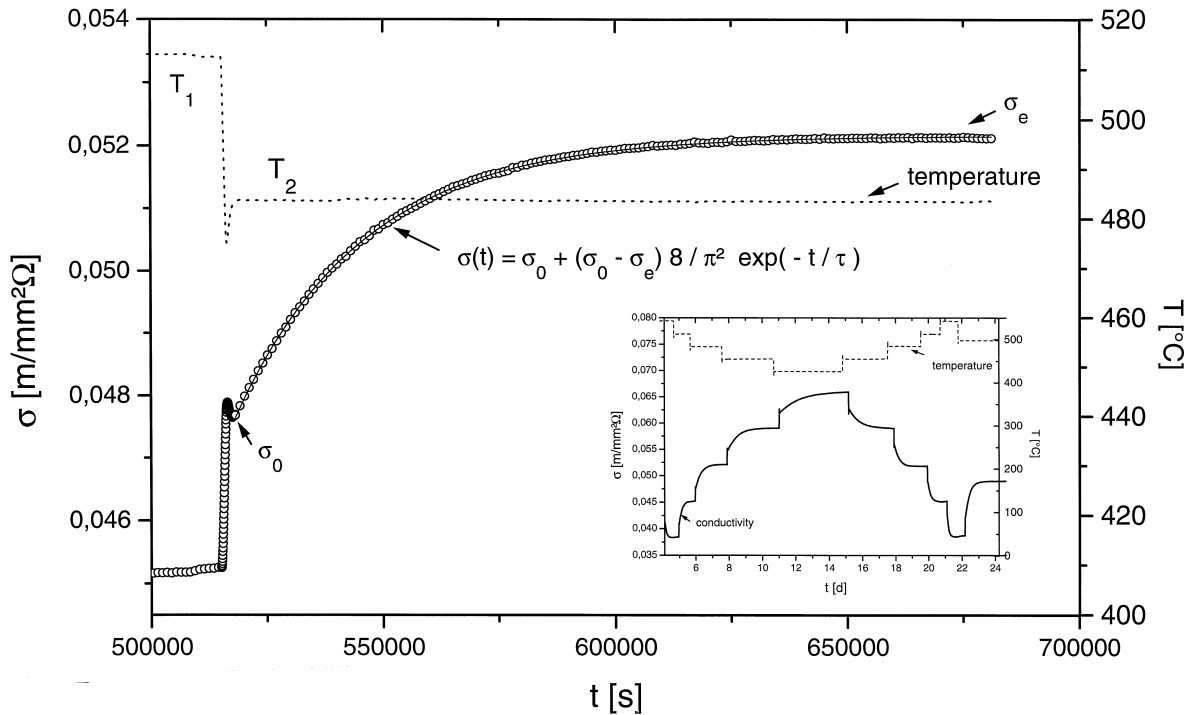


Fig. 2. Development of the conductivity with time by doing one temperature step (thin line: fit of Eq. (1)); the inset shows temperature and conductivity as a function of time over the whole duration of one experiment.

crystal width b . The time dependence of the oxygen concentration c is exactly described by the expression:

$$c(t) = c_0 + (c_0 - c_e) \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \times \exp\left\{-\left[\frac{(2i+1)\pi}{b}\right]^2 Dt\right\} \quad (1)$$

with c_0 starting oxygen concentration, c_e saturation oxygen concentration, D diffusion coefficient and t time. Considering for long times only the first dominant term of this sum yields as an approximation the equation:

$$c(t) = c_0 + (c_0 - c_e) \frac{8}{\pi^2} e^{-t/\tau} \text{ with } \tau = \frac{b^2}{\pi^2 D}. \quad (2)$$

From a fitting procedure (thin line in Fig. 2) we get the diffusion coefficient D as fitting parameter, if we substitute the concentration c by the corresponding values of the conductivity σ .

Such a substitution can be applied if there exists a linear relation between the oxygen content and the electrical conductivity. Claus et al. [13] showed that the conductivity is a good measure for the oxygen content in a range of $0 \leq \delta \leq 0.25$. Our measurements done in a temperature range of 390°C – 550°C at various oxygen partial pressures correspond to an oxygen content of ~ 6.98 – ~ 6.8 [14] in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals. There is no information about the oxygen concentration of the other measured $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples. However, the transition temperature T_c in dependence of annealing temperature T_a shows no difference for the $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals and only a little shift of 20 K to smaller values for $\text{DyBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals with respect to $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals [1]. Due to this and the results of Lindemer et al. [15] and Lindemer and Specht [16] where no difference in the dependence of the oxygen content from the annealing temperature for different rare earth atoms in $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples has been found, we conclude that oxygen content of the measured

$\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{DyBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples is the same as for the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples at identical annealing temperatures.

2.5. Determination of error

To improve the reproducibility of the diffusion coefficient measurements possible sources influencing the values of the diffusion coefficients were examined. We developed a simulation program for the oxygen diffusion based on a numerical solution of the diffusion equation in two dimensions (Fick's 2 law). If $\sigma(t)$ -curves exhibit deviations from the ideal shape shown in Fig. 2 it was checked if this deviation is due to temperature variations with time. For that reason the $\sigma(t)$ -curves were simulated with this program using the measured function of temperature vs. time. As long as this simulation represents the measured conductivity curve, one can be sure, that the crystal was not damaged. Otherwise the obtained results were discarded.

The applied diffusion model is based on infinite length of the crystal. Only in this case the amount of oxygen diffused along the length of the crystal can be neglected. With the simulation program we were able to estimate the error due to the finite dimensions of our samples. For example a ratio of the sample length to the sample width a/b of about 3 causes a difference of the diffusion coefficient of about 3.5%.

The numerical simulation is based on Eq. (1) which describes the situation correctly. Eq. (2), used for the fitting process, is an approximation. A comparison of the simulated $\sigma(t)$ -curve with the result of the fitting procedure shows only at the beginning of the diffusion process different slopes for both curves. After a time t' (estimated to about 2500 s) they were identical. The analysis of the $\sigma(t)$ -curves uses therefore only the measured values starting at the time t' for the fitting procedure leading to a reduction of the diffusion coefficient by about 2%.

The simulation of the diffusion process is also a tool to check the behavior of the oxygen content during the temperature ramp. The assumption that the temperature ramp is fast compared to the oxygen diffusion is not any longer valid. Our estimation yields that a concentration balancing of 10–20% occurred during the ramp time. This means we do not start with the ideal concentration distribution but

the evaluation of the data mentioned in the preceding paragraph considers this situation too.

We adjusted the annealing temperature from different starting temperatures. This results in an ensemble of diffusion coefficients for one annealing temperature. With the advanced measuring equipment and the consideration of the above given corrections we get now a final scattering of the diffusion coefficient of $\pm 3\%$. The evaluation of a diffusion coefficient from a single measuring curve can reach a standard deviation up to $\pm 5\%$.

During the measurement cycles the crystals were repeatedly equilibrated at one annealing temperature for controlling purposes. Since the equilibrium conductivity value at this controlling temperature remained constant for successive anneals irreversible damages on the crystals during the annealing process can be ruled out.

3. Results

3.1. In- and outdiffusion

As shown in our recent paper [2] the in- and outdiffusion processes have the same time constants for $\text{Gd}_{1-x}\text{Y}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals. To examine if the in- and outdiffusion are equally fast for other $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals as well we monitored for each of our samples in- and outdiffusion-curves at different annealing temperatures. Fig. 3 shows such curves at three different temperatures for a $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystal. It is clearly visible that the time constants for in- and outdiffusion have the same value at any annealing temperature. The equivalence of the time constants for in- and outdiffusion was found on all measured crystals independent of the rare earth central atom or different impurity level. Thus, oxygen in- and outdiffusion is not a surface controlled process, the values of the time constants only depending on the annealing temperature.

3.2. Temperature dependence

The diffusion coefficients for the $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals were determined between 390°C and 550°C. Within this range the temperature dependence

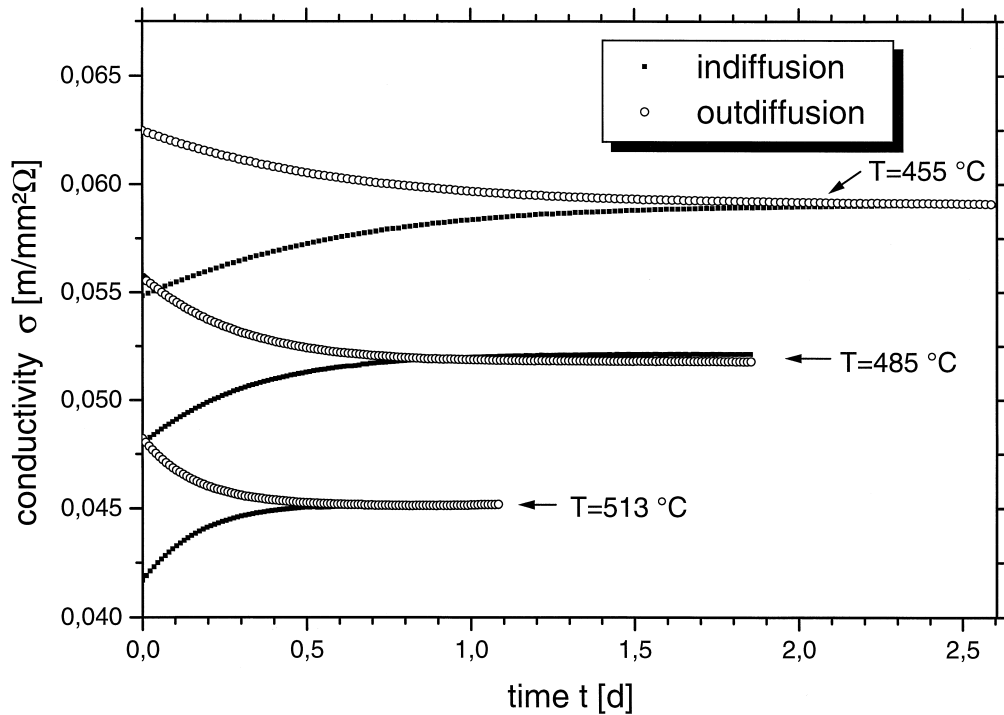


Fig. 3. Conductivity vs. time curves to reach the equilibrium conductivity value for three different annealing temperatures T_a .

of the diffusion coefficient $D(T)$ follows an Arrhenius-law for all crystals showing that the diffusion is a thermally activated process

$$D(T) = D_0 e^{-E_A/k_B T}$$

with D_0 preexponential factor, E_A activation energy, k_B Boltzmann constant and T temperature. Plotting $\ln D$ over the reciprocal temperature $1/T$ yields the activation energy E_A for oxygen diffusion from the slope of the regression line. In Fig. 4 such plots are given for six different $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals. The results for the temperature dependence of the $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{DyBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and Ca-doped $\text{Y}_{1-y}\text{Ca}_y\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals together with one of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystal (Y8) from Fig. 4 are shown in Fig. 5. All determined activation energies E_A and the pre-exponential factors D_0 are summarised in Table 1.

3.3. Oxygen partial pressure dependence

The equilibrium oxygen content of $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals is a function of the anneal-

ing temperature T_a and the oxygen partial pressure p_{O_2} . A study on this dependence is found for example at Lindemer et al. [14]. To check whether a variation of the diffusion coefficient with oxygen pressure exists, one $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystal (Y314) was measured at oxygen partial pressures of $p_{\text{O}_2} = 0.1, 0.5$ and 1 bar. In the inset of Fig. 6 the diffusion coefficients are plotted over the reciprocal temperature for these three oxygen partial pressures. The determination of the activation energies is done with an Arrhenius plot again and Fig. 6 shows this plot for an oxygen partial pressure $p_{\text{O}_2} = 0.1$ bar. In contradiction to the measurements at normal pressure (Figs. 4 and 5) the measuring points suggested to divide the investigated temperature range in two regions, first from 420°C – 460°C and second from 460°C – 520°C .

This splitting of the temperature range is equivalent with a splitting into two oxygen concentration regions [14], that means for the temperature range of 420°C – 460°C we get an oxygen content range of 6.95–6.90 and for 460°C – 520°C a range of 6.9–6.8. A regression curve for the two regions yields two

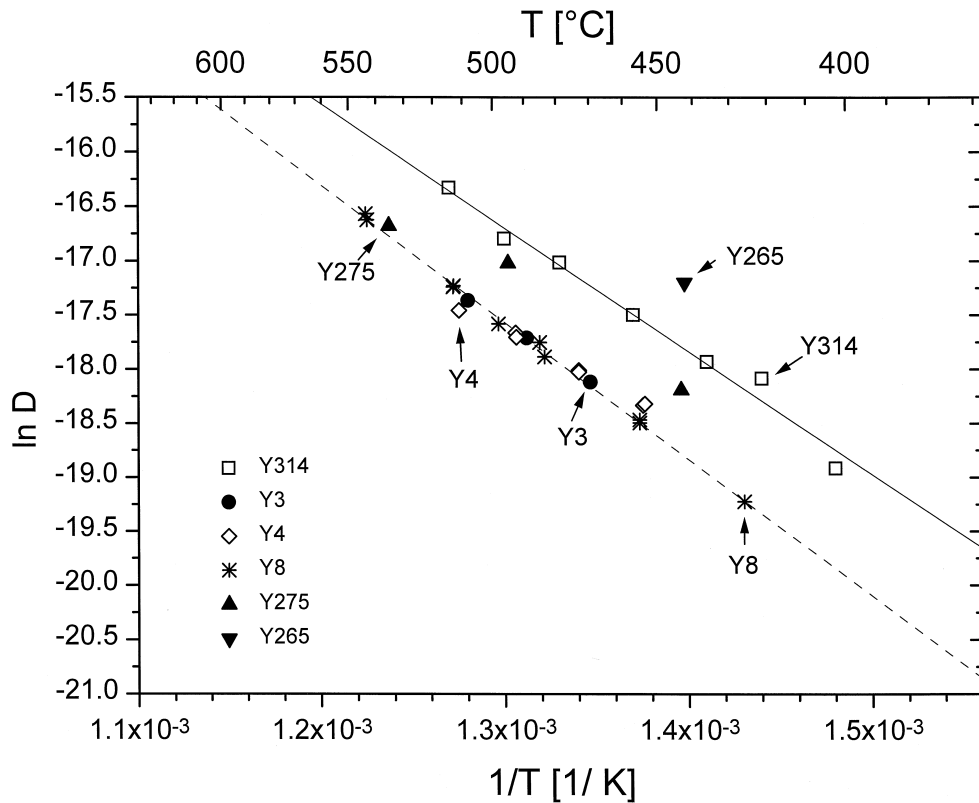


Fig. 4. Arrhenius plot of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals: triangles results from Ref. [2], all other from this paper.

different activation energies $E_A = 1.06$ eV and $E_A = 0.43$ eV (see Fig. 6).

3.4. Discussion

The values of the diffusion coefficient of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals presented in this paper are comparable with the results of the earlier paper. In the investigated temperature range of 390°C – 550°C the diffusion coefficient varied between 10^{-8} – 10^{-7} cm^2/s .

The comparison of the diffusion coefficients of the $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals with the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals reveals that the diffusion coefficients of all crystals are in the same range. No dependence of the diffusion coefficient from the rare earth atom has been found. Consequently the reported variation by up to two orders of magnitudes between different $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductors, deduced from rather indirect measurements of me-

chanical damping [3], is not confirmed by our results.

Additionally the mere speculation about the greatly enhanced oxygen mobility [4] in the crystals grown in BaZrO_3 -crucibles can be disproved by this results. As mentioned above all $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals are grown in ZrO_2 -crucibles. The impurity level of all these crystals is equal and amounts to about 1% Al on the Cu-chain sites as determined by microprobe analysis. On the other hand the crystals grown in BaZrO_3 crucibles contain no impurities down to 5 ppm level. The results of Figs. 4 and 5 show clearly that there exist no dependence of the diffusion coefficient from the impurity level within the accuracy of our measurements.

First investigations on Ca-doped $\text{Y}_{1-y}\text{Ca}_y\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals with $y = 0.1$ yield similar diffusion coefficients as the other samples. A change of the diffusion coefficient by Ca doping on the rare earth place is not expected, because the

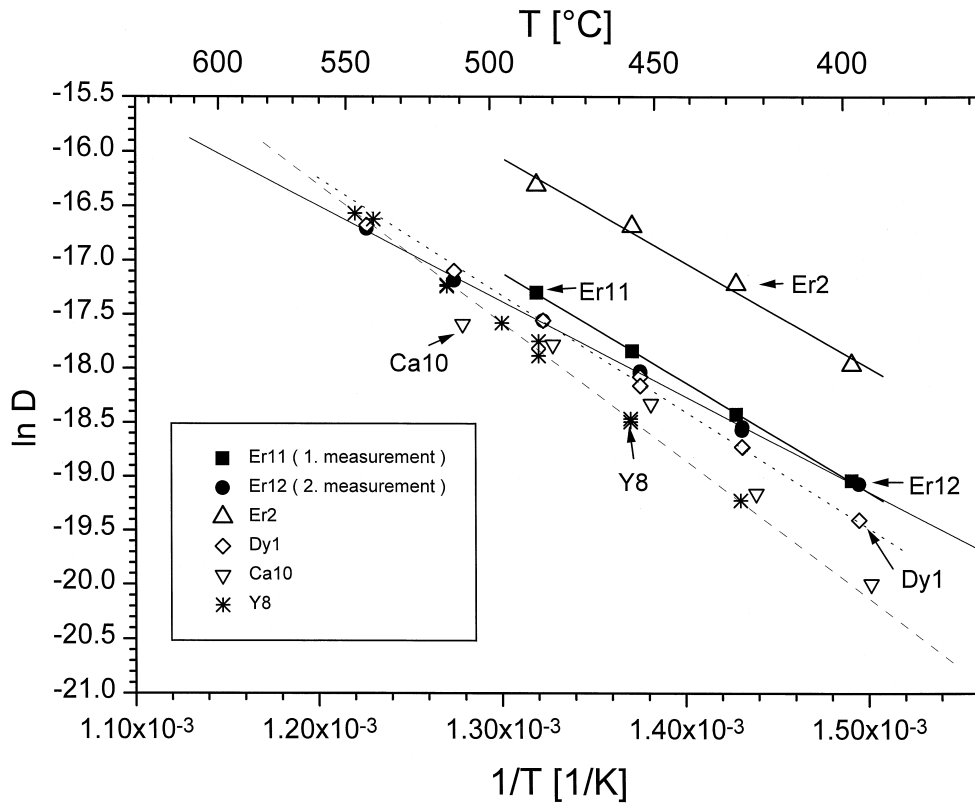


Fig. 5. Arrhenius plot of the $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{DyBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Y}_{1-y}\text{Ca}_y\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals in comparison with one $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystal from Fig. 4.

diffusion of the oxygen atoms in the Cu–O-chains takes place through thermally activated jumps over the so called O1- and O5-places.

Table 1
Activation energies, pre-exponential factor and ionic radius of the RE atom of the measured $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples and Ca-doped sample

Sample	RE atom	Ionic radius [Å]	E_A [eV]	D_0 [cm^2/s]
Y3	Y	0.93	0.975	0.057
Y4			0.764	2.2×10^{-3}
Y8			1.09	0.33
Y314			0.98	0.138
Er11	Er	0.88	0.875	0.02
Er12			0.76	2.71×10^{-3}
Er2			0.834	0.031
Dy1	Dy	0.91	0.93	0.038
Ca10	Y(90%), Ca(10%)	0.99	0.96	0.0475

To compare all published diffusion coefficients with our results Fig. 7 shows a summary of all these values (tracer diffusion coefficients are not considered). A comparison is often difficult because the measurements were done on ceramic samples or the tracer diffusion coefficient was determined. So the values of the chemical diffusion coefficients scatter up to seven orders of magnitudes and three orders of magnitudes for single crystals. A detailed discussion about the differences in the diffusion coefficients between the different groups is done in our earlier paper [2].

Even though we reached an accuracy of $\pm 5\%$ for the measurements of one single crystal, the results of different crystals show a scattering of up to $\pm 50\%$, most probably due to different microstructure, however ending the situation where even the order of magnitude has been uncertain.

In order to get an estimation in which way the contacting and stoving process influenced the crys-

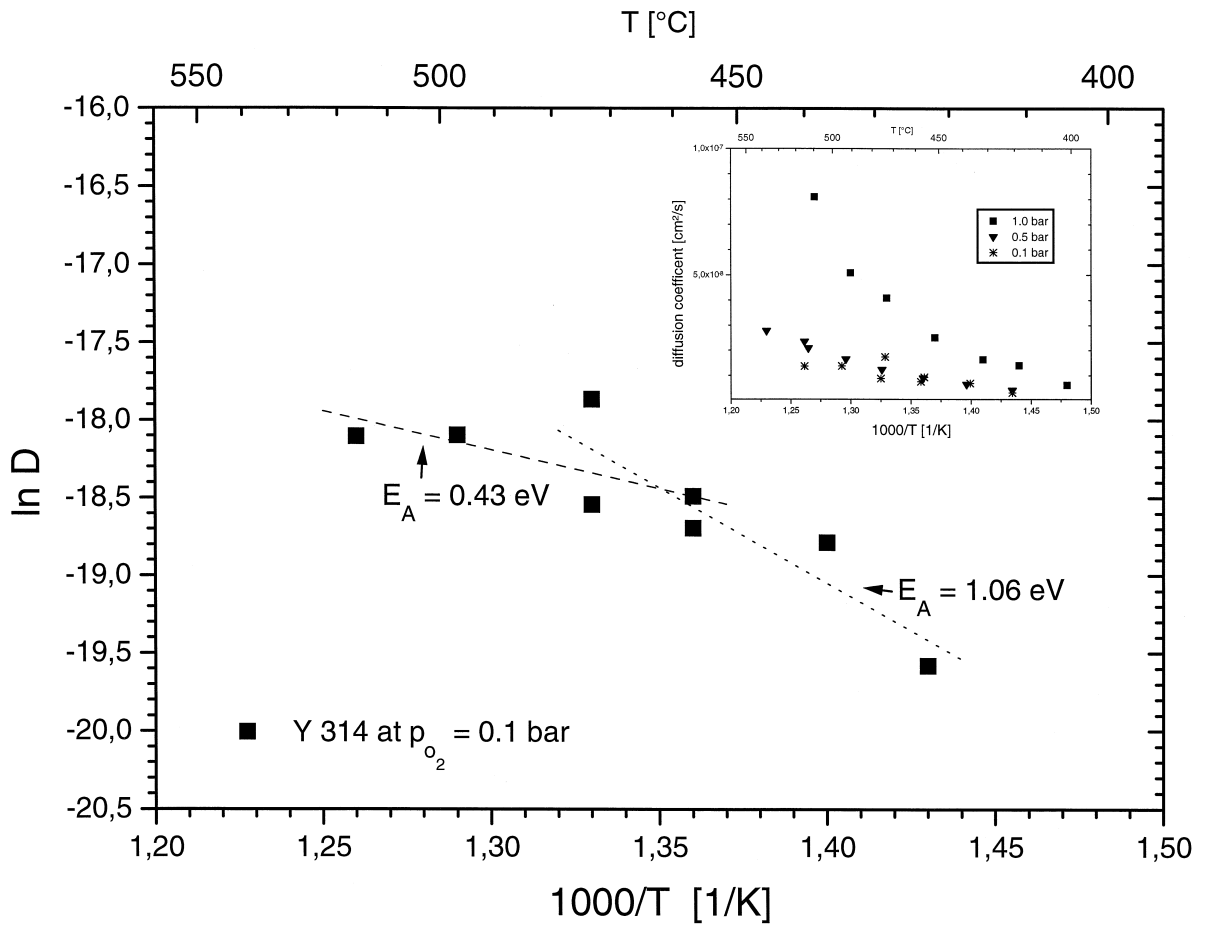


Fig. 6. Arrhenius plot of crystal Y314; measurements were done at a reduced oxygen partial pressure of 0.1 bar; the inset shows the $1/T$ dependence of the diffusion coefficient at three different oxygen partial pressures.

tals, crystal Er1 (see Fig. 5) was measured twice. The second preparation (polishing, contacting and stoving process) and measurement on this crystal Er1 leads to a diffusion coefficient which shows a slightly different slope in the Arrhenius plot. Starting from $400^{\circ}C$ with the same value both diffusion coefficients differ at $485^{\circ}C$ by about $\pm 10\%$. This might be due to the introduction of microcracks as well as due to changes in the crystal imperfections by the high temperature treatment.

This maximum scattering of $\pm 10\%$ from the second measurement cannot explain the scattering between the different crystals. Even for $ErBa_2Cu_3O_{7-\delta}$ samples from the same crystal growth batch the results show that each crystal has

its own quality in point of view of the oxygen diffusion. Possibly microcracks as well as flux inclusions are for the crystals different.

Summarising we state the overall accuracy of the diffusion coefficient for the $REBa_2Cu_3O_{7-\delta}$ single crystals is about $\pm 50\%$ due to the crystal imperfections although the accuracy of the diffusion coefficient for a single crystal is $\pm 5\%$.

Independent of the scattering of the diffusion coefficients for the preparation of samples for application this study enables us to calculate the times needed for homogeneous oxygenation of single crystals using the Einstein equation for the effective diffusion length $d_{eff} = \sqrt{6D(T)t}$. Note, that if the independence of the chemical diffusion coefficients

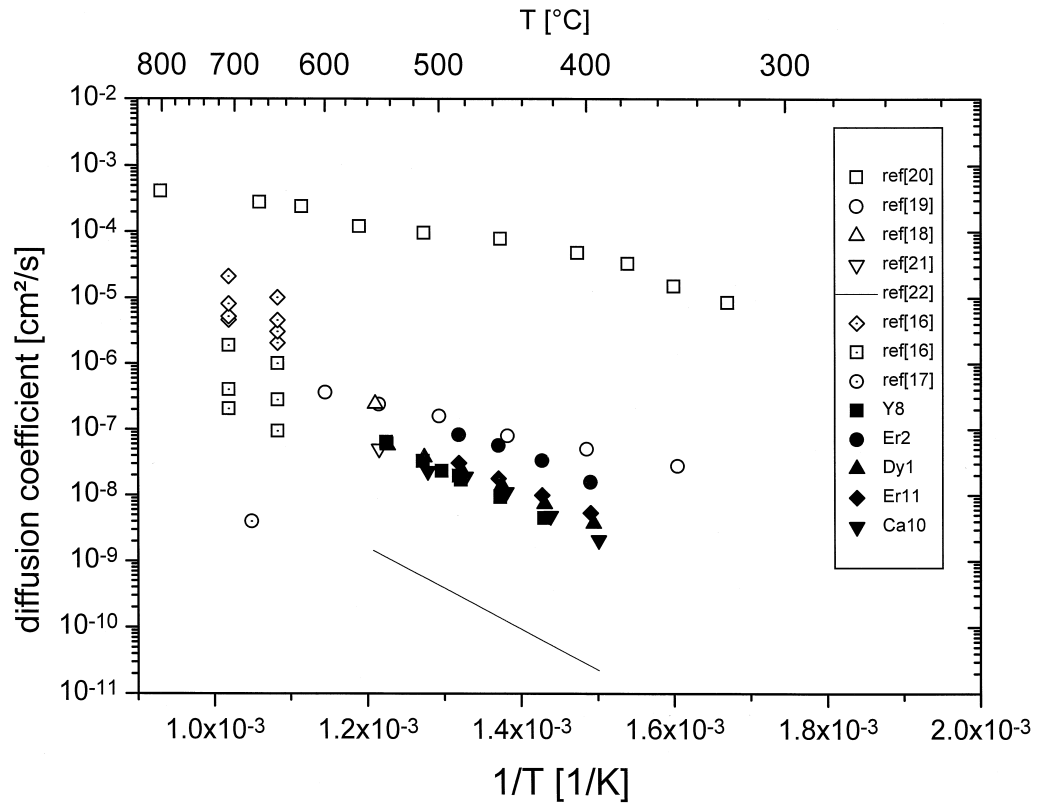


Fig. 7. A comparison of the chemical diffusion coefficients from the literature (open and line symbols: ceramic samples [17–21]; dotted symbols: single crystals [22,23]) with our results (full symbols).

from the rare earth element proven for Er, Dy and Gd can be extended to the lighter rare elements like Eu, Sm and Nd that there exists a major obstacle for the technical application of these compounds. Since their final oxygenation has to be performed at much lower temperature (e.g. around 300°C for the Nd and Sm compounds) the diffusion coefficients are about two orders of magnitude smaller than in the case of YBCO, prolonging the time for oxygenation by two orders of magnitude as well. So the increased oxygenation time by a factor of up to 100 for the Nd-123 system would prohibit the technical application of fully dense melt textured Nd samples.

As a consequence of the variation of the diffusion coefficients for different crystals, it is hard to determine an exact value for the activation energy. Table 1 reveals a deviation of the activation energy of about 30% for the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals.

Therefore it is only possible to fix regions for the activation energy E_A . So we determined E_A for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals in a range of 0.76–1.09 eV, for $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals in a range of 0.76–0.88 eV and for $\text{DyBa}_2\text{Cu}_3\text{O}_{7-\delta}$ a value of 0.93 eV. A dependence of the activation energy from the rare earth atom could not be found.

On the other hand the measurements on one of the crystals at different oxygen partial pressures (Fig. 6) may indicate a splitting of the measured values in two regions with $E_A \approx 1$ eV (for $\delta \leq 0.1$) and $E_A \approx 0.5$ eV (for $0.2 \geq \delta \geq 0.1$) respectively.

4. Conclusions

We measured the chemical diffusion coefficient of different $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals using in situ conductivity measurements during the oxygena-

tion process. For all crystals the time constant for the in- and outdiffusion process were equal at any annealing temperature and independent of the rare earth atom as well as from the impurity level.

The reproducibility of the diffusion coefficient for a single crystal is about $\pm 5\%$, however the scattering of the diffusion coefficients between different single crystals, even from the same batch are $\pm 50\%$. This difference is most probably caused by different crystal imperfections such as dislocations or microcracks.

The temperature dependence of the diffusion coefficient follows an Arrhenius law.

The activation energy is determined in a range of 0.76–1.09 eV independent of the rare earth atom, but there seems to be a dependence of the activation energy from the oxygen content of the samples.

Our results show on the one hand there is no influence of the used crucible material and therefore of the impurity level. That means the small amount of Al on the Cu-chain sites in all $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals does not change the value of the diffusion coefficient and thus the mobility of oxygen. On the other hand there exists within the accuracy of the measurement no dependence of the diffusion coefficient on the rare earth atom RE.

References

- [1] A. Erb, J.-Y. Genoud, M. Dhalle, F. Marti, E. Walker, R. Flükiger, *Appl. Superconductivity* 158 (1997) 1109.
- [2] A. Erb, B. Greb, G. Müller-Vogt, *Physica C* 259 (1996) 83.
- [3] J.L. Tallon, B.-E. Mellander, *Science* 258 (1992) 781.
- [4] D.A. Bonn, R. Liang, S. Kamal, A. Hosseini, W.N. Hardy, Surface impedance of high purity YBCO crystals grown in BaZrO_3 crucibles, Abstract of the APS meeting Los Angeles, 1998.
- [5] A. Erb, T. Traulsen, G. Müller-Vogt, *J. Cryst. Growth* 137 (1994) 487.
- [6] A. Erb, E. Walker, R. Flükiger, *Physica C* 245 (1995) 245.
- [7] A. Erb, E. Walker, J. Genoud, R. Flükiger, *Physica C* 282–287 (1997) 89.
- [8] W. Jost, K. Hauffe, *Diffusion*, Steinkopf Verlag, Darmstadt, 1972.
- [9] J. Crank, *The Mathematics of Diffusion*, Oxford Univ. Press, 1956.
- [10] S.J. Rothmann, J.L. Routbort, U. Welp, J.E. Baker, *Phys. Rev. B* 44 (5) (1991) 2326.
- [11] S.J. Rothmann, J.L. Routbort, J.E. Baker, *Phys. Rev. B* 40 (13) (1989) 8852.
- [12] S. Tsukui, T. Yamamoto et al., *Jpn. J. Appl. Phys. A* 30 (1991) 973.
- [13] H. Claus, M. Braun, A. Erb, K. Röhberg, B. Runtsch, H. Wühl, G. Bräuchle, P. Schweiss, G. Müller-Vogt, H.v. Löhneysen, *Physica C* 171 (1992) 42.
- [14] T.B. Lindemer, J.F. Hunley, J.E. Gates, A.L. Sutton, J. Brynstad, C.R. Hubbard, *J. Am. Ceram. Soc.* 72 (10) (1989) 1775–1788.
- [15] T.B. Lindemer, E.D. Specht, P.M. Martin, M.L. Flitcroft, *Physica C* 255 (1995) 65.
- [16] T.B. Lindemer, E.D. Specht, *Physica C* 268 (1996) 271.
- [17] K. Kishio, K. Suzuki, T. Hasegawa, T. Yamamoto, K. Kitazawa, K. Fucki, *J. Sol. State Chem.* 82 (1989) 192.
- [18] J.R. LaGraff, D.A. Payne, *Phys. Rev. B* 47 (1993) 3380.
- [19] S. Elschner, W. Becker, H. Bestgen, M. Brand, *Physica C* 202 (1992) 401.
- [20] E.J.M. O'Sullivan, B.P. Chang, *Appl. Phys. Lett.* 52 (1988) 1441.
- [21] A.P. Mozhaev, S.V. Chernyav, T.I. Udaltsova, N.M. Kotov, *J. Inorg. Chem* 37 (1992) 1111.
- [22] J.R. LaGraff, D.A. Payne, *Physica C* 212 (1993) 478.
- [23] A.T. Fiory, S. Martin, F. Schneemeyer, R.M. Fleming, A.E. White, *Phys. Rev. B* 38 (1988) 7129.