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OXYGEN DIFFUSION AND ISOTOPE EXCHANGE BEHAVIOUR OF $NdBa_2Cu_3O_{7-x}$

E. Kemnitz[1], *A. A. Galkin*[2], *T. Olesch*[3], *S. Scheurell*[1], *A. P. Mozhaev*[2] *and G. N. Mazo*[2]

[1]Institut für Chemie, Humboldt-Universität zu Berlin, Hessische Str. 1/2, 10115 Berlin
[2]Moscow State University, Department of Inorganic Chemistry, 119899 Moscow, Russia
[3]AERES Angewandte Umweltforschung GmbH, Rudower Chaussee 5, 12484 Berlin, Germany

Abstract

The oxygen diffusion and exchange behaviour of $NdBa_2Cu_3O_{7-x}$ is investigated by means of isothermal and dynamic-thermal analytical techniques. From the results it is concluded that oxygen anions move along vacancies in the CuO_2-layers of the perovskite-like structure. In temperature regions where the diffusion rate is low ($665 K < T < 773 K$) heterogeneous oxygen exchange reactions take place on the phase boundary. The higher the exchange rate the more the partially heterogeneous exchange is favoured in comparison to the completely heterogeneous isotope exchange. Depending on the oxygen deficiency of $NdBa_2Cu_3O_{7-x}$ the out-diffusion of oxygen becomes dominating at higher temperatures.

Keywords: diffusion, isotope exchange, mechanism, neodym barium cuprate

Introduction

High-T_c superconducting oxides of the composition $RBa_2Cu_3O_{7-x}$ (R– rare earth metal) crystallise in an oxygen-deficient layer structure with perovskite-like symmetry. The oxygen content of such cuprates may be varied between $0 \le x \le 1$ without damaging the perovskite structure. However, it has been proven by numerous X-ray and neutron diffraction analytical studies that 123 phases undergo an orthorhombic to tetragonal phase transition (OT transition) if the oxygen content falls below a certain value of $x \sim 0.5$ [1, 2]. Simultaneously, superconductivity disappears and the tetragonal cuprates exhibit antiferromagnetic and semiconducting properties. The critical oxygen content where the transition occurs depends on several parameters (rare earth metal, annealing conditions etc.) affecting the thermodynamics and kinetics of the phase transition. Thus, the OT transition takes place at $x \sim 0.65$ for $YBa_2Cu_3O_{7-x}$ whereas tetragonal $NdBa_2Cu_3O_{7-x}$ is formed at x–0.45 already [2]. Considering the crucial effect of the oxygen content on the properties of $RBa_2Cu_3O_{7-x}$ the detailed knowledge of the oxygen diffusion behaviour is of particular importance for the preparation of materials with well-defined properties. The oxygen mobility in $YBa_2Cu_3O_{7-x}$ was thoroughly investigated by means of isothermal measuring techniques [3–10]. Unfortunately, diffusion coefficients and ac-

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tion energies determined as a function of different parameters (T, p_{O_2}, oxygen deficiency x) do not correspond to each other very well. Considerable differences may arise from different principles of measurement as well as from microstructural peculiarities of the 123 phases. Additional information on the diffusion behaviour and the interactions between solid cuprates and the gas phase can be received from dynamic-thermal experiments. For this purpose a technique has been developed where the oxygen exchange between the solid oxide and an ^{18}O enriched gas phase is analysed by means of mass spectrometry [11]. From the variation of the isotopic composition of the gas phase it is possible to draw conclusions on the mechanism of oxygen exchange and diffusion on the basis of the model of Musikantov *et al.* [12]. Moreover, temperature regions of enhanced oxygen mobility can be determined using the very sensitive method.

Here, we report on the investigation of the oxygen diffusion and exchange behaviour of $NdBa_2Cu_3O_{7-x}$ using dynamic-thermal and isothermal techniques. The combination of two complementary methods enables us to discuss quantitative (D, E_a) as well as qualitative (mechanism) aspects of oxygen diffusion processes. The Nd system is known to be more stable than the Y-123 phases, and it exhibits very high critical current densities in single crystals [13]. In spite of the considerable differences between the ionic radii Nd may occupy Ba sites resulting in the formation of solid solutions of the composition $Nd_{1+z}Ba_{2-z}Cu_3O_{7-x}$ with a large variety of z [14].

Experimental

Samples of $NdBa_2Cu_3O_{7-x}$ were prepared by the conventional solid-state reaction between Nd_2O_3 (99.9%, Aldrich), $BaCO_3$ (99.99%, Aldrich) and CuO (99.98%, Aldrich). The starting materials were mixed in a vibrating mill and pressed into pellets of 10 mm diameter. The pellets were sintered for 50 h at 1123 K interrupted by three intermediate grindings. After this the samples were reground and annealed for 20 h at 623 K in flowing O_2. The phase purity of $NdBa_2Cu_3O_{7-x}$ was checked by XRD using a Guinier-de Wolff camera (Enraf-Nonius) at CuK_α radiation. The oxygen content of the samples was determined by iodometric titration [15]. Diffusion coefficients were calculated from the results of a coulometric titration technique introduced by Mozhaev *et al.* [6, 7]. About 70 mg of the sample were placed into a sample chamber under constant oxygen partial pressure and heated up to starting temperature between 623 and 673 K. After the equilibrium between the solid and the gas phase was achieved the temperature was rapidly increased by 20 K and the quantity of desorbed oxygen was detected by a coulometric cell based on a CaO stabilised ZrO_2 electrode. This procedure was repeated in intervals of 20 K up to the thermal decomposition of the 123 phases. A detailed description of the method is given elsewhere [6].

The dynamic-thermal isotopic exchange between the cuprates and the ^{18}O enriched gas phase was investigated in a special glass vessel with separate control valves for the isotope gases $^{32}O_2$ (99.95%, Messer-Griessheim) and $^{36}O_2$ (99.9%, IC Chemikalien). 600 mg of the sample were put on a sample holder consisting of several plates in order to ensure the maximal contact between the solid and the gas phase. The sample was heated from room temperature to 773 K by a constant heating rate of 10 K min^{-1}. The initial oxygen partial pressure was adjusted to 40 Pa with a mole ratio of $^{36}O_2$:$^{32}O_2$=3:1. The concentrations of all oxygen containing molecules in the system (H_2O, $^{32}O_2$, $^{34}O_2$, $^{36}O_2$ and CO_2) were detected by a quadrupole mass spectrometer (Balzers, QMG 421 I).

Before starting, it is necessary to remove adsorbed molecules such as H_2O and CO_2 from the solid surface which disturb the oxygen isotope exchange during the measurement. For this purpose the samples have to be heated up to 573 K for at least 2 h at a pressure of 10 Pa. Usually, the temperature and time were chosen in such way that the oxygen content of the sample remains unchanged during the isothermal pre-treatment.

On the methods

The coulometric titration method

The coulometric titration method is an evolved gas analytical technique which has been developed for determining diffusion coefficients in high-T_c superconducting cuprates by Mozhaev *et al.* [6, 7]. The quantity of oxygen desorbed from a solid oxide during isothermal annealing is determined as a function of time. Diffusion coefficients are obtained from the experimental correlation between the conversion α and the reaction time. The calculation is based on Fick's 2nd law for spherical particles (Eq. (1)).

$$\frac{c-c_f}{c_0-c_f}=\frac{6}{\pi^2}\sum_{n=1}^{n=\infty}\left[\frac{1}{n^2}\right]\exp\left[\frac{-n^2\pi^2D^2\tau}{r^2}\right] \tag{1}$$

r radius of a spherical particle
τ time of the isothermal heat treatment
c actual oxygen concentration ($\tau>0$) in a spherical particle
c_0 initial oxygen concentration ($\tau=0$) in a spherical particle
c_f final oxygen concentration ($\tau=\tau_{eq}$) in a spherical particle
D diffusion coefficient; $D=D_0\exp(-E_a/RT)$

The calculation programme is based on an iterative method. Further mathematical and experimental details are given elsewhere [6, 7]. On account of the very high sensitivity of the coulometric cell it is possible to detect slight changes of the oxygen partial pressure of the gas phase. Therefore, diffusion coefficients of $RBa_2Cu_3O_{7-x}$ can be calculated from a variation of the oxygen content of $\Delta x\geq0.02$ mole per formula unit. The result is not affected by desorbed CO_2 or H_2O as D values obtained from thermogravimetric techniques nor by traces of impurities ($BaCuO_2$, 211 phase etc.) which do not release oxygen during the measurement. In combination with isothermal heating the coulometric titration method enables us to determine quantitative diffusion parameters (D, E_a etc.) of $RBa_2Cu_3O_{7-x}$ as a function of temperature and the partial oxygen pressure. Usually, the volume diffusion of oxygen anions is slow in comparison to the oxygen exchange reactions on the solid-gas phase boundary. For this reason the time required for the establishment of equilibrium between the whole bulk and the gas phase is between 1 and 3 h depending on the temperature of isothermal heating and the particle size of the analysed powder. The rate of the release of oxygen decreases with growing grain size of the sample resulting in the corresponding correlation between the experimental D values and the granulometric composition of the samples [6, 7]. In contrast to the isothermal method with dynamic-thermal isotope exchange measurements the interactions between the surface layers of the oxocuprates and the gas phase are detected. Consequently, the isotope exchange equilibrium is already achieved after less than 20 min.

Dynamic-thermal isotope exchange

As a result of the reaction between an ^{16}O containing solid oxide and an ^{18}O enriched gas phase three different types of oxygen molecules can be observed in the gas phase: $^{32}O_2={}^{16}O^{16}O$, $^{34}O_2={}^{18}O^{16}O$ and $^{36}O_2={}^{18}O^{18}O$. The isotopic composition is changed by diffusion and oxygen exchange processes:

(i) the escape of oxygen from the solid to the gas phase (out-diffusion)

(ii) the incorporation of oxygen from the gas phase into the solid structure (in-diffusion)

(iii) the homogeneous oxygen exchange between $^{32}O_2$ and $^{36}O_2$ catalysed by the solid surface

(iv) the partially heterogeneous oxygen exchange

(v) the completely heterogeneous oxygen exchange

These processes may take place separately or simultaneously depending on the analysed compound and the temperature. For this reason it is necessary to define appropriate coefficients to be able to distinguish between simultaneously occurring reactions [11, 12].

$$s=\frac{\left\{\left[^{32}O_2\right]+\left[^{34}O_2\right]+\left[^{36}O_2\right]\right\}_{t=i}}{\left\{\left[^{32}O_2\right]+\left[^{34}O_2\right]+\left[^{36}O_2\right]\right\}_{t=o}}=\frac{p_i}{p_o} \tag{2}$$

The coefficient s corresponds to the measured sum of partial oxygen pressures standardised to the initial value. It can be changed by diffusion processes only (Table 1).

$$c=\frac{\left[\frac{^{34}O_2}{2}\right]+\left[^{36}O_2\right]}{\left[^{32}O_2\right]+\left[^{34}O_2\right]+\left[^{36}O_2\right]} \tag{3}$$

The coefficient c is a measure of the relative ^{18}O content in the gas phase. The value of c decreases as a result of out-diffusion and heterogeneous exchange processes. It is independent of the rate of the homogeneous isotope exchange (Table 1).

$$y=\left\{\frac{\left[{}^{34}O_2\right]}{\left[{}^{32}O_2\right]+\left[{}^{34}O_2\right]+\left[{}^{36}O_2\right]}\right\}_{eq}-\left\{\frac{\left[{}^{34}O_2\right]}{\left[{}^{32}O_2\right]+\left[{}^{34}O_2\right]+\left[{}^{36}O_2\right]}\right\}_{t=i} \tag{4}$$

The coefficient y describes the deviation of the isotopic composition of the gas phase from the equilibrium state. This deviation is represented by the difference between the $^{34}O_2$ content at equilibrium and the $^{34}O_2$ content measured at $t=i$. Hence, y approaches to zero if $^{34}O_2$ is formed by isotope exchange reactions.

$$v=\left\{\frac{\left[\frac{{}^{34}O_2}{2}\right]}{\left[\frac{{}^{34}O_2}{2}\right]+\left[{}^{36}O_2\right]}\right\}_{t=i}\left\{\frac{\left[\frac{{}^{34}O_2}{2}\right]+\left[{}^{36}O_2\right]}{\left[\frac{{}^{34}O_2}{2}\right]}\right\}_{t=o} \tag{5}$$

The coefficient v is a measure of the $^{34}O_2$ partial pressure relative to the sum of ^{18}O containing oxygen. A significant increase of v arises from the occurrence of all oxygen exchange reactions. However, v is nearly unaffected by diffusion processes on account of the fact that v does not depend on the $^{32}O_2$ content.

The reaction between the ^{16}O containing solid oxide and the ^{18}O enriched gas phase leads to the variation of the isotopic composition of the gas phase during the dynamic-thermal heating process. The resulting variation of the coefficients (Eqs (2–5)) is detected as a function of temperature. From these plots of s, c, y and v *vs.* T it is possible to conclude which diffusion and exchange processes take place in a certain temperature range (Table 1). It is reasonable to discuss the changes of the coefficients assuming that no isotope effect occurs in view of the rather high oxygen exchange activity and the high number of oxygen vacancies in the perovskite-like cuprates.

Before analysing powdered samples the influence of the measuring conditions on the results has to be studied thoroughly [11]. First, it has been verified that the composition of the gas phase ($^{36}O_2$:$^{32}O_2$ as 3:1; p_{O_2}=10–200 Pa) remains constant during heating the empty glass vessel up to 823 K. The influence of the heating rate, the oxygen pressure and the initial ratio of $^{32}O_2$:$^{34}O_2$:$^{36}O_2$ is described on the example of yttrium cuprates. A heating rate of 10 K min^{-1} and an oxygen pressure of 40 Pa have been established to be appropriate conditions for highly sensitive and reproducible measurements [11]. The effect of the grain size on the results of the dynamic-thermal measurements is less significant than that observed for the determination of diffusion coefficients. Since with the isotope exchange experiments the

Table 1 Possible diffusion processes and isotope exchange reactions between a ^{16}O containing solid oxide and an ^{18}O enriched gas phase. The variation of the coefficients resulting from the individual processes is predicted provided that no isotopic effect occurs

Process, reaction on the phase boundary	Resulting variation of the coefficients
out-diffusion: oxygen is released from the solid $2\,^{16}O(s) \rightarrow {}^{32}O_2(g)$ (the ^{18}O content of the solid can be neglected, so that only $^{32}O_2$ is released)	s increases c decreases as long as $^{32}O_2$ is primarily released y increases since the relative amount of $^{34}O_2$ in the gas phase is reduced v remains unchanged
in-diffusion: incorporation of oxygen ($^{32}O_2$, $^{34}O_2$ and $^{36}O_2$) from the gas phase into the solid $^{32}O_2(g) \rightarrow {}^{16}O(s) + {}^{16}O(s)$ $^{34}O_2(g) \rightarrow {}^{16}O(s) + {}^{18}O(s)$ $^{36}O_2(g) \rightarrow {}^{18}O(s) + {}^{18}O(s)$	s decreases c is nearly constant y remains unexchanged owing to the constant relative $^{34}O_2$ content of the gas phase v slight increase (the reduction of $[^{36}O_2]$ dominates the nearly negligible decrease of $[^{34}O_2]$)
homogeneous isotope exchange reaction $^{32}O_2(g) + {}^{36}O_2(g) \rightarrow 2\,^{34}O_2(g)$	s remains unchanged c is constant because of $[^{36}O_2] = -[^{34}O_2]/2$ y decreases ($[^{34}O_2]$ approaches the equilibrium concentration) v increases due to the formation of $^{34}O_2$

Table 1 Continued

Process, reaction on the phase boundary	Resulting variation of the coefficients
partially heterogeneous isotope exchange $^{36}O_2(g) + {}^{16}O(s) \rightarrow {}^{34}O_2(g) + {}^{18}O(s)$ $2\,^{34}O_2(g) + 2\,^{16}O(s) \begin{array}{l} \nearrow {}^{32}O_2(g) + {}^{18}O(s) \\ \searrow {}^{34}O_2(g) + {}^{16}O(s) \end{array}$	s remains unchanged c decreases (the loss of $^{36}O_2$ is not compensated by the formation of $^{34}O_2/2$) y decreases because of the formation of $^{34}O_2$ v increases rapidly as a result of the conversion of $^{36}O_2$ to $^{34}O_2$
completely heterogeneous isotope exchange $^{36}O_2(g) + 2\,^{16}O(s) \rightarrow {}^{32}O_2(g) + 2\,^{18}O(s)$ $^{34}O_2(g) + 2\,^{16}O(s) \rightarrow {}^{32}O_2(g) + {}^{18}O(s) + {}^{16}O(s)$	s remains unchanged c decreases since $^{36}O_2$ is consumed but $^{34}O_2$ is not formed y is nearly constant (a slight increase may arise from the reaction between $^{34}O_2$ and the solid) v increases owing to the dominating reduction of the $^{36}O_2$ content

reaction between the surface layers of the solid oxide and the gas phase is investigated this method is primarily aimed to determine temperature regions of enhanced oxygen mobility and exchange activity, respectively. It is obvious that due to the decrease of the oxygen generation rate with growing grain size the dimension of the variation of the isotopic composition is affected by the particle size of the analysed powder. On the other hand, the onset temperatures of the measured effects are independent of the grain size if the method is sensitive enough to detect even slight changes of the isotope ratio $^{32}O_2$:$^{34}O_2$:$^{36}O_2$ as in the case of mass spectrometry.

Hence, the ^{18}O isotope exchange technique applies to all solid oxides which are not irreversibly decomposed during the low oxygen pressure annealing treatment. Although no quantitative parameters of oxygen diffusion can be determined it is possible to characterise the diffusion and exchange behaviour of the analysed compounds depending on the composition and structural properties of the solid oxide. However, it is necessary to keep the measuring conditions constant in order to be able to compare the properties of different samples and to prevent a misinterpretation of the measured effects. The diagrams obtained for different Y-123 phases were very characteristic and enabled us to identify X-ray amorphous $YBa_2Cu_3O_{7-x}$ after a thermal treatment in oxidising and non-oxidising gas atmosphere [11].

Results and discussion

Figure 1 depicts the values of diffusion coefficients of $NdBa_2Cu_3O_{7-x}$ (particle size between 10 and 50 μm) depending on the temperature at different oxygen partial pressures. Similar to other perovskite-like cuprates oxygen diffusion occurs very fast in $NdBa_2Cu_3O_{7-x}$. The experimental D values are even higher than those obtained for the Y-123 phases under identical conditions [6, 7], probably resulting from the more defective structure of $NdBa_2Cu_3O_{7-x}$. The activation energies of diffusion at low oxygen pressures are smaller than the E_a values obtained from the Arrhenius plots at higher p_{O_2} (Fig. 2). It should be noted that the number of vacancies in $NdBa_2Cu_3O_{7-x}$ decreases with growing partial oxygen pressure in the gas phase. Therefore, the results above are in complete agreement with the widely accepted vacancy mechanism of oxygen diffusion in perovskite-like cuprates [4–7, 9–11, 16]. On the other hand, the diffusion coefficients seem to decrease with $\log p_{O_2}$ (Fig. 1) which is difficult to explain in terms of the vacancy mechanism. An inherent feature of evolved gas analytical methods is assumed to be responsible for the observed variation of $\log D$ with p_{O_2}. Diffusion coefficients of solid materials are calculated from compositional changes of the gas phase, i.e. from the oxygen desorption rate and the time required for the establishment of equilibrium. It is apparent that the quantity of oxygen desorbed in a certain time increases with the extra oxygen content of cuprates. On account of the decreasing amount of mobile oxygen it becomes understandable why the calculated D values are diminished at low oxygen pressures in spite of the rising number of vacancies in the CuO_2-layers.

In order to get further information on the mechanism of the oxygen exchange process on the surface of $NdBa_2Cu_3O_{7-x}$ dynamic-thermal experiments were per-

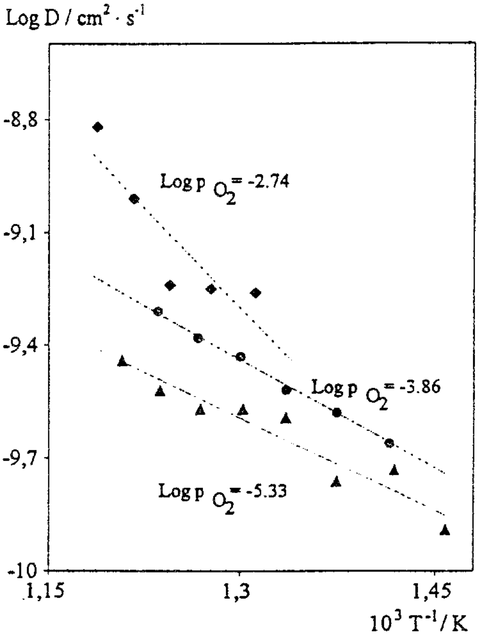

Fig. 1 Correlation between the oxygen diffusion coefficients of $NdBa_2Cu_3O_{7-x}$ and the reciprocal temperature at different oxygen partial pressures. The oxygen deficiency x increases with growing temperature and decreasing p_{O_2}

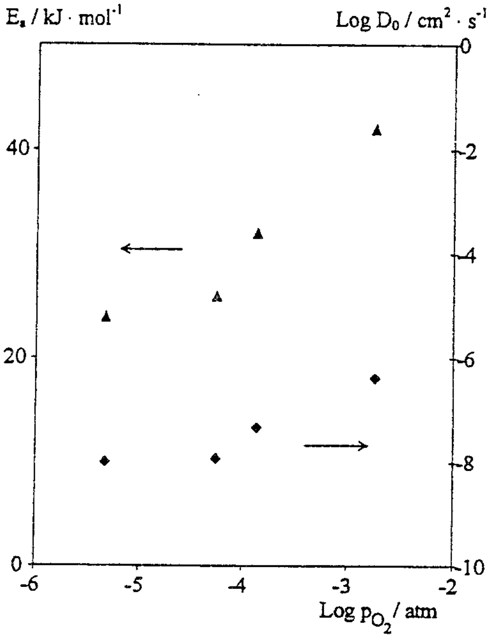

Fig. 2 Calculated values of the activation energy of oxygen diffusion and the preexponential factor depending on the oxygen partial pressure during the isothermal measurement

formed. For the Nd-123 phase the isothermal pre-treatment was performed at 773 K and at a $^{32}O_2$ pressure of 40 Pa. After this the system was evacuated and cooled down rapidly to 300 K. This isothermal pretreatment changes the composition of the $NdBa_2Cu_3O_{6.76}$ to oxygen-deficient orthorhombic $NdBa_2Cu_3O_{6.55}$

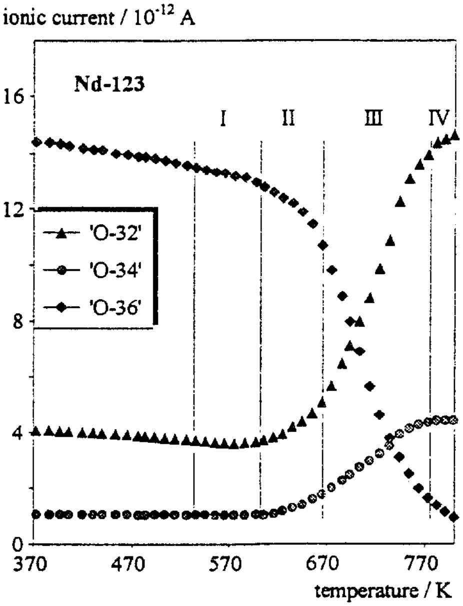

Fig. 3 Change of the isotopic composition of the gas phase during the reaction with orthorhombic oxygen-deficient $NdBa_2Cu_3O_{6.55}$

Figure 3 illustrates the variation of the isotopic composition of the gas phase during the reaction with $NdBa_2Cu_3O_{6.55}$ as a function of temperature. It can be seen that isotope exchange reactions start to occur above 600 K indicated by the significant reduction of the $^{36}O_2$ content which is accompanied by the formation of $^{34}O_2$ and $^{32}O_2$. Above 760 K the $^{34}O_2$ concentration is constant whereas $[^{36}O_2]$ approaches to zero. More detailed conclusions can be drawn from Figs 4 and 5 illustrating the variation of the coefficients s, c, y and v with growing temperature. Four temperature regions can be defined corresponding to the onset-temperatures of characteristic changes of the coefficients resulting from diffusion or exchange processes.

Region I (535 K<T<605 K)

The decrease of s above 535 K is suggestive for the capture of oxygen from the gas phase into the solid. The coefficients c and y remain unchanged below 605 K on account of the fact that the three types of oxygen molecules ($^{32}O_2$, $^{34}O_2$ and $^{36}O_2$) are incorporated into the structure with the same reaction rate. The slight increase of v (Fig. 4) can also be explained by the in-diffusion of oxygen. As long as no exchange reactions occur the $^{34}O_2$ concentration is very small in comparison to the

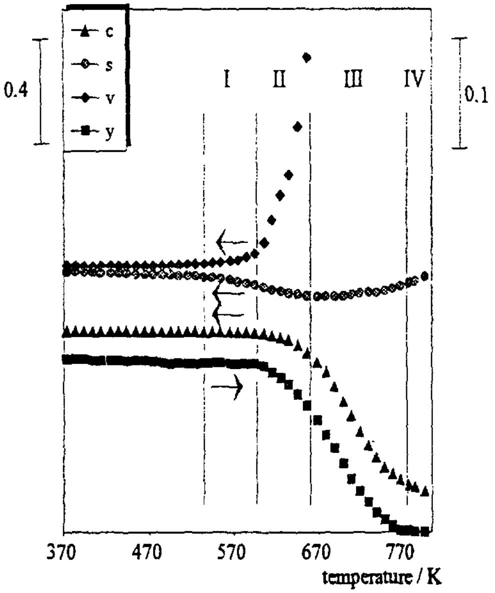

Fig. 4 Temperature-dependent variation of the coefficients *s*, *c*, *y* and *v* during the reaction between orthorhombic oxygen-deficient $NdBa_2Cu_3O_{6.55}$ and ^{18}O enriched oxygen

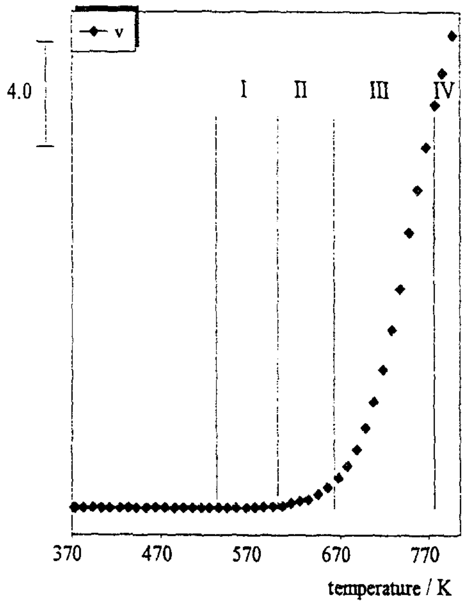

Fig. 5 Variation of the coefficient *v* during the reaction between orthorhombic oxygen-deficient $NdBa_2Cu_3O_{6.55}$ and ^{18}O enriched oxygen as a function of the temperature

$^{36}O_2$ content. Consequently, the nearly negligible decrease of $[^{34}O_2]/2$ does not affect v significantly, and the slightly growing coefficient v arises from the in-diffusion of $^{36}O_2$ only. Moreover, from Fig. 5 it can be seen that the increase of v in the first temperature region is negligible. Consequently, it is evident that neither homogeneous nor heterogeneous isotope exchange processes take place between orthorhombic oxygen-deficient $NdBa_2Cu_3O_{6.55}$ and oxygen below 605 K, after the thermal pre-treatment at 773 K as described above.

Region II (605 K<T<665 K)

The coefficient s continues diminishing up to 665 K as a result of further capture of oxygen from the gas phase into the solid structure. Remarkably, the quantity of oxygen entering the bulk is rather low in spite of the considerable oxygen deficiency of the Nd-123 phase. The variation of s is quite moderate, and it does not exceed ±10% during the whole measurement. In addition to s the coefficients c and y start to decrease above 605 K due to the reduction of the ^{18}O content in the gas phase and the formation of $^{34}O_2$. That means that isotope exchange reactions occur although the oxygen exchange rate is rather slow below 665 K as indicated by the relatively slight increase of v (Fig. 5). On account of the small variation especially of c and y it is difficult to conclude which exchange process is favoured in this temperature region. Remarkably, $^{32}O_2$ is formed above 605 K whereas the total oxygen pressure decreases (Fig. 3). This effect can be explained by the occurrence of the completely heterogeneous isotope exchange only. However, the decrease of the coefficient y suggests that both heterogeneous exchange processes take place simultaneously (Table 1). In contrast to this, the homogeneous exchange reaction can be neglected considering the small increase of the $^{34}O_2$ concentration below 665 K.

Region III (665 K<T<773 K)

At the beginning of the third temperature region the coefficient s is approximately constant suggesting that the quantity of oxygen from the gas phase incorporated into the solid is almost equal to the quantity of $^{32}O_2$ released from the cuprate. Hence, between 665 and 726 K opposite diffusion processes occur with the same rate. Above 726 K the out-diffusion becomes dominating and s rises continuously.

In contrast to s the other coefficients c, y and v vary substantially in this temperature region. From the accelerated formation of $^{34}O_2$ and $^{32}O_2$ (Fig. 3) it is deduced that the oxygen exchange rate is very high. The considerable increase of v as well as the rapid fall of c and y suggest that the partially heterogeneous isotope exchange is dominating in comparison to the other exchange and diffusion processes. However, at the end of the third temperature region the smaller decrease of y indicates that the completely heterogeneous isotope exchange is enhanced again. Simultaneously, the formation of $^{34}O_2$ is decelerated (Fig. 3), i.e. the contribution of the homogeneous exchange is insignificant at higher temperatures, too.

Region IV (773 K<T<813 K)

Above 773 K the $^{34}O_2$ concentration achieves the equilibrium value and y becomes zero. The coefficient c decreases slightly whereas v continues rising (Figs 4 and 5). Taking into account the constant value of $y=0$ it is evident that the completely heterogeneous exchange is the only reaction responsible for the observed variation of c, y and v. In addition to this exchange process $^{32}O_2$ is released from the Nd-123 phase indicated by the significant increase of s. These conclusions are in full agreement with the variation of the isotopic composition (Fig. 3). The $^{34}O_2$ content remains constant, so that homogeneous as well as partially heterogeneous isotope exchange reactions can be excluded. This $^{34}O_2$ concentration may be regarded as equilibrium value. It has to be referred to the fact that this equilibrium state is determined by the measuring conditions as for instance the initial quantities of $^{32}O_2$ and $^{36}O_2$ or the heating rate. Nevertheless, it is obvious that the completely heterogeneous oxygen exchange is favoured if the exchange rate between the solid and the gas phase is limited as already observed in the low temperature region between 535 and 605 K. At temperatures above 820 K $^{36}O_2$ is exhausted and no more isotope exchange reactions would be detected.

Conclusions

The coulometric titration method as well as the dynamic-thermal isotope exchange have been proved to be appropriate techniques for characterising the oxygen diffusion and isotope exchange behaviour of $NdBa_2Cu_3O_{7-x}$. From isothermal measurements it can be deduced that oxygen ions move along vacancies in the CuO_2-layers similar to the diffusion mechanism in $YBa_2Cu_3O_{7-x}$. Dynamic-thermal experiments show that heterogeneous but nearly no homogeneous oxygen exchange reactions take place simultaneously with diffusion processes. The highest exchange rate is observed between 665 and 773 K where the partially heterogeneous exchange is dominating. Hence, the oxygen mobility in $NdBa_2Cu_3O_{7-x}$ is high in this temperature region although the oxygen pressure of the gas phase (coefficient s) does not vary significantly. The completely heterogeneous oxygen exchange is favoured if the exchange rate is limited by experimental conditions such as low temperature or a lack of $^{36}O_2$ in the gas phase.

At higher temperatures oxygen is released from $NdBa_2Cu_3O_{7-x}$ with a desorption rate depending on the temperature, the partial oxygen pressure and the total pressure of the gas phase as well as on the composition of the 123 phase. A detailed study on the effect of the oxygen deficiency x and the degree of substitution of barium by neodymium z on the diffusion and exchange behaviour of $Nd_{1+z}Ba_{2-z}Cu_3O_{7-x}$ is in progress. We will report on the results very soon.

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