An experimental study of copper self-diffusion in CuO, $Y_2Cu_2O_5$ and $YBa_2Cu_3O_{7-x}$ by secondary neutral mass spectrometry

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Copper self-diffusion has been studied in CuO, $Y_2Cu_2O_5$ and $YBa_2Cu_3O_{7-x}$ ceramics by the SNMS (secondary neutral mass spectrometry) technique in the temperature range 700–900 °C with the stable isotope ^{63}Cu used as a tracer. The lowest diffusion rate and the highest value of activation energy were found for the $Y_2Cu_2O_5$ phase. Copper self-diffusion was also studied along the *c* axis of $YBa_2Cu_3O_{7-x}$ single crystals. It was shown that the anisotropy of Cu diffusion in $YBa_2Cu_3O_{7-x}$ is rather high. The diffusion rate in the *c* direction of single crystals is more than two orders of magnitude lower than that in ceramic samples.

Since the discovery of high-temperature superconductivity a number of experimental studies have been concerned with mass transport in superconducting oxides. The most common method applied involved a study of the diffusion of radioactive tracers and the use of different sectioning methods or SIMS (secondary ion mass spectrometry) for the determination of depth profiles. In this work we tried to apply a relatively new method of depth profile analysis, plasma-SNMS, that has emerged as a result of the development of SIMS. The former has two advantages in comparison to SIMS. First, a very low energy of primary ions (several hundred eV) allows the performance of depth profiling with very high depth resolution, which is especially valuable for the analysis of mass transport in thin films and heterostructures. Secondly, relatively easy quantification of the data is possible, as SNMS is less matrix-dependent than SIMS.

Experimental

Polycrystalline $Y_2Cu_2O_5$ was synthesized by the conventional ceramic process starting from Y_2O_3 and CuO. $Y_2Cu_2O_5$ and CuO 'low density' ceramic substrates were prepared by conventional sintering at 1050 and 950 °C, respectively. The final density of these substrates was around 90% of the theoretical values for $Y_2Cu_2O_5$ and CuO. The average grain size was *ca.* 10 µm for the both specimens.

High-density CuO substrates were prepared by hot pressing (pressure 4 GPa, temperature 700 °C, duration 60 min). The density reached in this case was 97%. It was not possible to estimate the grain size from SEM photographs. The density of substrates was determined by picnometric weighing in CBr_3H. The uncertainty of this procedure was determined as ±1% (absolute) by using Ge single crystals as a reference material.

CuO substrates were pre-annealed in an oxygen flow prior to polishing to avoid possible reduction of copper.

The single crystals of the $YBa_2Cu_3O_{7-x}$ phase were grown from a melt of composition 3:25:72% ($YO_{1.5}$–$BaCO_3$–CuO). The mixture was heated in an alumina crucible to 1000 °C and cooled to room temperature at the rate of 1–5 °C h^{-1}. Single crystals were separated by breaking apart the crucible.

EPMA (electron probe microanalysis) was performed with an accuracy better than 1%, using a CAMECA analyzer and showed that the crystals had the stoichiometric composition.

The diffusion couples were prepared by deposition of thin films of CuO enriched with the stable isotope ^{63}Cu onto the surface of polished ceramic substrates. The roughness of the substrates before the deposition was between 0.1 and 0.2 µm as a determined by the profilometer Talystep (Rank–Taylor–Hobson). The films were deposited by RF sputtering using thick-film ^{63}CuO targets. The ratio of copper isotopes $^{63}Cu/^{65}Cu$ in the films was 95/5. The ratio of copper isotopes $^{63}Cu/^{65}Cu$ in the substrates was 69/31 (the natural ratio).

The 'film' copper with an isotope ratio $^{63}Cu/^{65}Cu = 95/5$ was used as a tracer in this work.

To study the anisotropy of copper diffusion in $YBa_2Cu_3O_{7-x}$ the same films were deposited on the (001) surface of $YBa_2Cu_3O_{7-x}$ single crystals (the size of the crystals was *ca.* 3 × 3 × 0.1 mm). For $YBa_2Cu_3O_{7-x}$ all diffusion annealings were performed in an oxygen flow, and for $Y_2Cu_2O_5$ and CuO in air.

Depth profile analyses of the diffusion couples were performed by the SNMS technique in direct bombardment mode (DBM) using an INA-3 set-up (Leybold AG). In this experimental mode the low pressure Kr (Ar) plasma in the analysis chamber of the spectrometer is supported by electron-cyclotron resonance. The sample is situated inside the plasma and separated from it by a grounded aperture. The primary ions are extracted from the plasma volume by a negative voltage applied to the sample surface (600 V in our case). These ions are used for the sputtering of the sample. Neutral particles generated in the course of the sputtering have to travel approximately 5 cm through the plasma to the entrance of the ion optics. This distance is long enough for effective post-ionization by plasma electrons. If plasma parameters, sample holder assembly and the extraction voltage applied to the sample are properly adjusted, very high depth resolution can be achieved (up to 2–5 nm).[1]

Some problems related to sample charging arise in the course of the analysis of insulating materials ($Y_2Cu_2O_5$ in our case). The depth profiling of $^{63}CuO/Y_2Cu_2O_5$ diffusion couples was performed with a Ni grid (grid period = 50 µm) pressed onto the sample surface by a mask. The profilometric measurements confirmed the rectangular shape of the small craters restricted by conductive stripes of the grid and the uniform depth of these craters over the ion bombarded area (typically 1–2 mm in diameter).

The following working parameters of SNMS analysis were used: RF power = 150 W; Kr (Ar) pressure = 3.0×10^{-3} mbar; Helmholtz coil current = 4.9 A and accelerating potential for the primary ions = 600 V.

Discussion

The experimental procedures employed in this work are quite different from the traditional and very well developed methods of diffusion experiments such as techniques using radioactive tracers and serial sectioning for depth profiling.[2,3]

The first problem related to the application of thin film diffusion couples is that the thin film, which actually is the source of the tracer, constitutes approximately a quarter of the whole diffusion profile. Moreover it would be advisable to perform some correction for differences in sputtering rates between substrates and films.

However, our preliminary studies showed that the sputtering rates for CuO, $Y_2Cu_2O_5$ and $YBa_2Cu_3O_{7-x}$ do not differ by more than 25–30%. So the average sputtering rate was applied for the transformation of sputtering time into depth.

The other problem that arises in the case of thin film diffusion couples is related to the grain growth. The temperature of CuO deposition was relatively low (400 °C) and insufficient to allow perfectly crystalline material. Intensive grain growth during the first few minutes of a diffusion annealing under elevated temperature changes the surface morphology and the resultant broadening of transitions between layers in an experimental SNMS depth profile is caused not only by mass transport but also by recrystallization. It is almost impossible to separate these two processes.

Taking this effect into account all diffusion couples were pre-annealed at 800 °C for 1–3 min. The depth profiles of copper isotopes in these pre-annealed samples were used as the starting point for further calculations.

The depth profiles of 'film' copper in the starting samples before diffusion annealings were not step-like. To correct this the 'additional time' was calculated in the following way. In the first stage the copper diffusion coefficient was calculated assuming that the initial profile was step-like. Then the calculated diffusion coefficient was used to estimate the time that would be necessary to allow the development of the real initial profile starting from an ideal one. In the next stage the sum of 'additional time' and the real time of a diffusion annealing was applied for the calculation of the copper diffusion coefficient. As a rule after four to seven iterations both 'additional time' and the diffusion coefficient stop changing. The final diffusion coefficients were on average two to three times lower than the ones calculated under the assumption of an ideal shape of the initial diffusion profile.

Results

An experimental study of copper self-diffusion in CuO

The first series of experiments was performed with 'low density' CuO polycrystal substrates. The average grain size for the substrate material was *ca.* 10 µm and the thickness of the ^{63}CuO film was *ca.* 1 µm. The diffusion profiles were simulated using the error function solution of the Fick's second law equation for the case of contact of two semi-infinite bodies where $C(x,t)$ = concentration of the tracer, D = copper diffusion coefficient and x' = the thickness of the CuO film.

$$C(x,t)=A\{1-\mathrm{erf}[(x-x')/(4\mathrm{Dt})^{1/2}]\} \qquad (1)$$

An experimental profile in this diffusion couple at 800 °C and annealing time of 20 min is shown in Fig. 1. The parameters A, x' and D were chosen to minimize the value of χ^2, the measure of the goodness of the fit. χ^2 values were in the range 0.5–2. The position of the film/substrate boundary was determined by the position of the 50% point of the 'film' copper diffusion profile. Calculated values of copper self-diffusion coefficients are given in Table 1 together with the errors determined in the course of fitting.

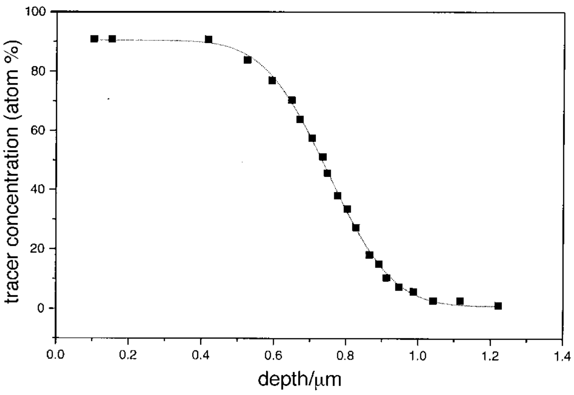

Fig. 1 Experimental points and simulated curve for 'film' copper diffusion profile in a CuO/CuO diffusion couple ('low density' substrate) annealed for 20 min at 800 °C

Table 1 Copper diffusion coefficients in polycrystal CuO samples

T/°C; t/min of diffusion experiment	D/cm^2 s^{-1} high density (97%)	D/cm^2 s^{-1} low density (90%)
850; 10		$(8.4\pm0.2)\times10^{-14}$
800; 10	$(2.3\pm0.7)\times10^{-14}$	$(4.8\pm0.4)\times10^{-14}$
800; 20		$(4.0\pm0.2)\times10^{-14}$
750; 15		$(1.5\pm0.1)\times10^{-14}$
750; 30		$(1.7\pm0.08)\times10^{-14}$
700; 15	$(3.6\pm0.8)\times10^{-15}$	
700; 30	$(3.6\pm0.8)\times10^{-15}$	$(2.8\pm0.2)\times10^{-15}$
700; 60		$(5.8\pm0.2)\times10^{-15}$
650; 30	$(1.6\pm0.1)\times10^{-15}$	
650; 60	$(2.3\pm0.1)\times10^{-15}$	
600; 30	$(4.0\pm0.4)\times10^{-16}$	
600; 60	$(4.4\pm0.4)\times10^{-16}$	

The second series of diffusion experiments was performed with 'high-density' substrates (97% of the theoretical value) prepared by hot-pressing. In this case it was not possible to simulate the whole diffusion profile by a simple error function. A combined fitting function with an additional term corresponding to grain-boundary diffusion was applied in this case [eqn. (2)]

$$C(x,t)=A\{1-\mathrm{erf}[(x-x')/(4Dt)^{1/2}]\}+C\exp[-B(x-x')^{6/5}] \qquad (2)$$

In this experimental series the thickness of ^{63}CuO films was *ca.* 0.3 µm and as a consequence the surface concentration of the tracer decreased in the course of the diffusion annealings. Experimental diffusion profiles at 700 °C of 'film' copper are shown in Fig. 2. It is clearly seen that the concentration in the films is uniform but decreases with increasing diffusion time. This means that diffusion in the film is much quicker than in the substrate, probably due to higher defect concentration.

This uniform decrease of the tracer concentration in the film means that the Gaussian term for volume diffusion is more appropriate for the description of volume diffusion than the error function term. However, application of eqn. (3) does not change the calculated values of the copper diffusion coefficients by more than a factor of two.

$$C(x,t)=A\exp[-(x-x')^2/4Dt]+C\exp[-B(x-x')^{6/5}] \qquad (3)$$

The temperature dependences of copper self-diffusion coefficients for both series of experiments are compared in Fig. 3 and Table 1 and the data are fitted to an Arrenius equation [eqn. (4)]

$$D=D_0\exp(E_a/RT) \qquad (4)$$

where E_a is the activation energy and D_0 is the intercept.

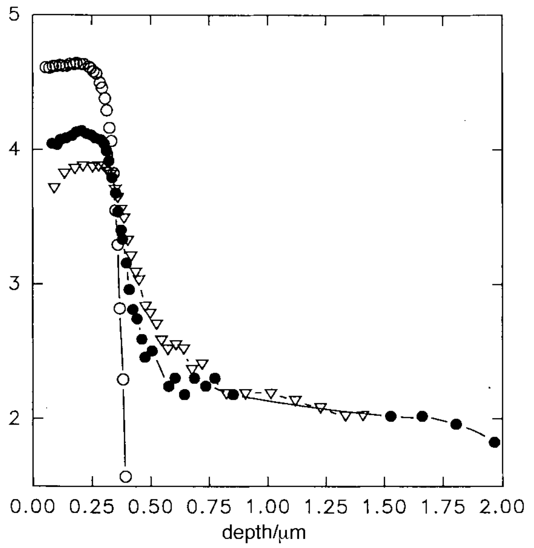

Fig. 2 Experimental SNMS profiles of 'film' copper in a CuO/CuO diffusion couple ('high density' substrate). Filled circles, before annealing; open circles, after 15 min annealing at 700 °C; triangles, after 30 min annealing at 700 °C.

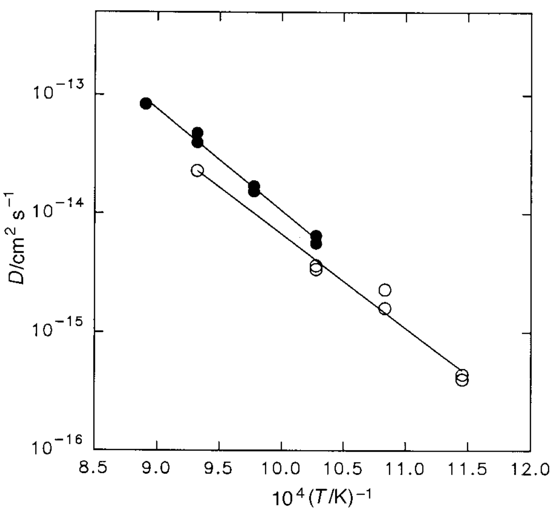

Fig. 3 The temperature dependence of the copper self-diffusion coefficient in CuO determined for 'low' (●; $E_a = 162 \pm 7$ kJ mol^{-1}) and 'high density' (○; $E_a = 150 \pm 15$ kJ mol^{-1}) substrates

Both absolute values of diffusion coefficients and activation energies are in good agreement.

The literature data shows that CuO is non-stoichiometric, most probably due to cation vacancies[4] as in other divalent oxides of the elements of the first transition series such as NiO, CoO and FeO. Hence the very low value of the intercept (5×10^{-6}–5×10^{-7} cm^2 s^{-1}) for the temperature dependence of the copper self-diffusion coefficient can be considered as a consequence of a vacancy diffusion mechanism in CuO. This mechanism of cation diffusion has also been established for NiO and CoO.[5] However the values of the intercept for NiO and CoO (5×10^{-2} and 5×10^{-3} cm^2 s^{-1}, respectively)[6] are much higher than that found for CuO. Such a difference can be caused by different types of crystal structures: the rocksalt structure of NiO and CoO differs from the structure of CuO.

Copper self-diffusion in $Y_2Cu_2O_5$ polycrystals

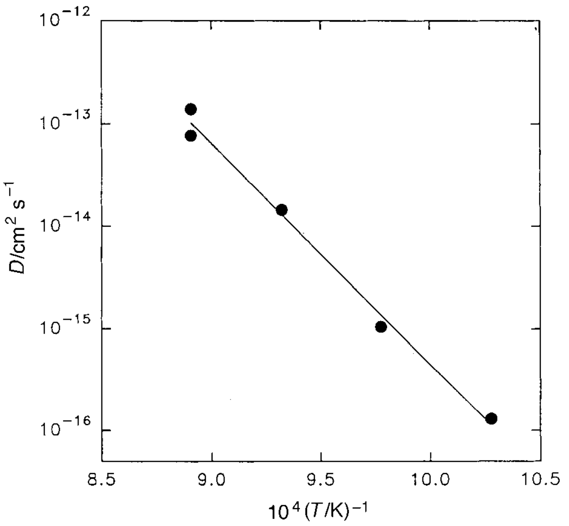

Fig. 4 The temperature dependence of the copper self-diffusion coefficient in $Y_2Cu_2O_5$ ($E_a = 415 \pm 20$ kJ mol^{-1})

Table 2 Copper diffusion coefficients in a polycrystal $Y_2Cu_2O_5$ sample

temp./°C; time of diffusion experiment	D/cm^2 s^{-1}
850; 10 min	$(1.4 \pm 0.1) \times 10^{-13}$
850; 30 min	$(7.7 \pm 0.6) \times 10^{-14}$
800; 190 min	$(1.5 \pm 0.2) \times 10^{-14}$
750; 21 h	$(1.0 \pm 0.2) \times 10^{-15}$
700; 76 h	$(1.4 \pm 0.2) \times 10^{-16}$

The same experimental procedures were applied to study of copper self-diffusion in $Y_2Cu_2O_5$ and the data obtained are presented in Fig. 4 and Table 2. The activation energy of copper diffusion in this phase is almost twice as large as that in $YBa_2Cu_3O_{7-x}$ and even more than twice the value for CuO. At the same time the absolute values of diffusion coefficients are the lowest for the temperature range studied.

The structure of $Y_2Cu_2O_5$ can be considered as a stack of Cu—O layers parallel to the *ab*-plane, separated by layers of YO_6 octahedra. Copper atoms have distorted square-pyramidal coordination (Cu—O distance around 2 Å) with a fifth oxygen atom at a distance of 2.8 Å.[7,8]

The copper diffusion mechanism in $Y_2Cu_2O_5$ is probably rather complex. First, there are no data in the literature on any cation or oxygen non-stoichiometry of this phase. As a consequence the concentration of vacancies might be much lower than that in CuO or $YBa_2Cu_3O_{7-x}$. Secondly, the value of intercept (Table 3), which is proportional to the entropy of diffusion, is too high even for an interstitial mechanism. The value of intercept for interstitial diffusion in metals is in the range 10^{-3}–1 cm^2 s^{-1}.[9]

Experimental study of anisotropy of copper diffusion in $YBa_2Cu_3O_{7-x}$

The last set of experiments was performed with $YBa_2Cu_3O_{7-x}$ single crystals.

Table 3 Activation energies and pre-exponentials of the temperature dependences of copper self-diffusion coefficients in CuO, $YBa_2Cu_3O_{7-x}$ and $Y_2Cu_2O_5$

sample	E_a/kJ mol^{-1}	$\log_{10}$ (D_0/cm^2 s^{-1})
CuO (97%)	150 ± 15	-6.1 ± 0.9
CuO (90%)	162 ± 7	-5.5 ± 0.4
$YBa_2Cu_3O_{7-x}$ (polycrystal)	240 ± 9	-0.65 ± 0.4
$YBa_2Cu_3O_{7-x}$ (crystal *c* axis)	280 ± 30	-1.3 ± 1.5
$Y_2Cu_2O_5$	415 ± 20	6.3 ± 0.9

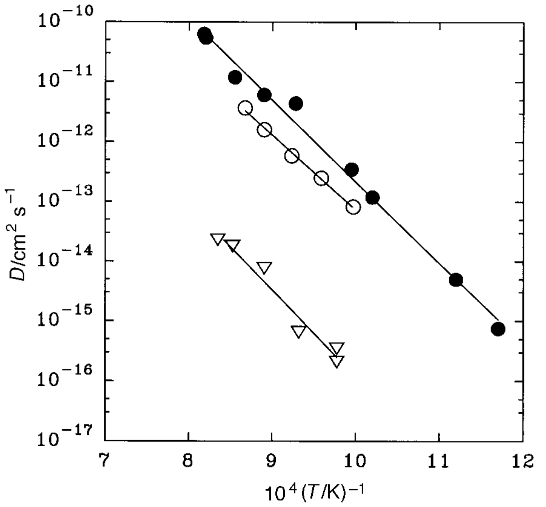

Fig. 5 The temperature dependence of the copper self-diffusion coefficient in $YBa_2Cu_3O_{7-x}$. Filled circles, literature data for $YBa_2Cu_3O_{7-x}$ polycrystals ($E_a = 256 \pm 4$ kJ mol^{-1}); open circles, our data for ceramic $YBa_2Cu_3O_{7-x}$ samples ($E_a = 240 \pm 9$ kJ mol^{-1}); triangles, copper self-diffusion coefficients along the c axis of $YBa_2Cu_3O_{7-x}$ single crystals ($E_a = 280 \pm 35$ kJ mol^{-1}).

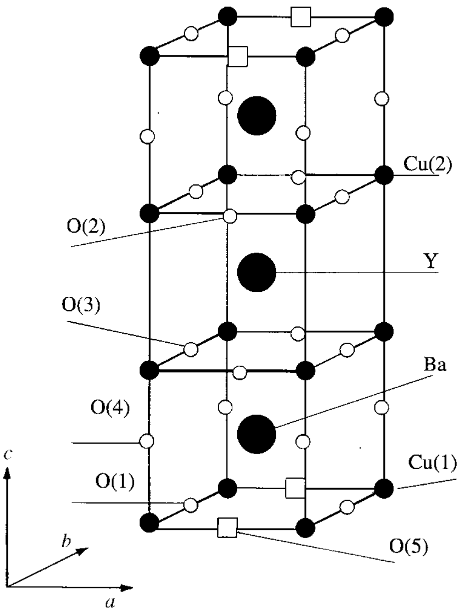

Fig. 6 The structure of $YBa_2Cu_3O_{7-x}$

The data on copper diffusion in $YBa_2Cu_3O_{7-x}$ found in the literature[10] and obtained in the course of our studies[11] are shown in Fig. 5. The good agreement between our data and literature data for polycrystalline samples gives us faith in our experimental procedures. The new data on copper diffusion along the c axis are also presented in Table 4.

The anisotropy of copper self-diffusion in this phase is surprisingly large. The ratio D_{poly}/D_c is estimated to be 200–400 (D_c = cation diffusion coefficient along the c axis). This result can be explained in the following way. The layers of square pyramids CuO_5, separated by yttrium ions, are presumed to be rigid. No additional ordering or disordering at elevated temperatures was observed in these layers. On the other hand, O(1) atoms are very mobile and statistically distributed between O(1) and O(5) positions (Fig. 6) under the conditions of the diffusion experiments. This is confirmed by very high anisotropy of oxygen diffusion in $YBa_2Cu_3O_{7-x}$ (four to six orders of magnitude).[12]

Gupta *et al.*[13] suggested that the most probable mechanism of copper diffusion in $YBa_2Cu_3O_{7-x}$ is *via* vacancies. The negatively charged copper vacancies that inevitably exist in the lattice will attract highly mobile and positively charged oxygen vacancies in the Cu(1)—O(1) layer. As a consequence the energy barrier for a copper atom to jump onto an adjacent vacant Cu(1) position will be significantly lower than that for a jump onto a Cu(2) vacancy.

The available data on the anisotropy of cation diffusion in $YBa_2Cu_3O_{7-x}$ are summarised in Table 5.

In spite of large absolute value, the anisotropy of copper diffusion is lower than the anisotropy measured for Ba diffusion.[14] For Ba, D_{poly}/D_c is at least 3000–4000, *i.e.* one order of magnitude higher. The authors of ref. 14 emphasise that this value represents a lower limit for the anisotropy of Ba diffusion as the measurements were performed on melt-textured ceramic samples rather than single crystals. The actual value of the anisotropy could be even larger as there is no continuous chain of Ba positions in $YBa_2Cu_3O_{7-x}$ along the c axis and diffusing in this direction Ba has to substitute for Y.

Table 4 Copper diffusion coefficients along the c axis of $YBa_2Cu_3O_{7-x}$ single crystals

temp./°C; t/h of diffusion experiment	D^a/cm^2 s^{-1}
925; 4	$(2.3 \pm 0.3) \times 10^{-14}$
900; 4	$(1.8 \pm 0.2) \times 10^{-14}$
850; 5	$(7.7 \pm 0.5) \times 10^{-15}$
800; 10	$(6.5 \pm 0.7) \times 10^{-16}$
750; 17	$(2.1 \pm 0.3) \times 10^{-16}$
750; 36	$(3.5 \pm 0.3) \times 10^{-16}$

[a] Two exponential functions.

Table 5 The anisotropy of cation diffusion in $YBa_2Cu_3O_{7-x}$

cation	D_{poly}/D_c	ref.
Ba	1000	14
Cu	200–400	this work
Ni	50–60	10,13
Co	1000	10

The anisotropy of Co diffusion measured by Routbort *et al.*[10] is of the same order of magnitude as that for Ba. He suggested that the reason for this is that Co preferentially substitutes only for copper in the position Cu(1), as confirmed by neutron diffraction. As a consequence the jump distance along c axis is at least two times longer than the ab plane.

Conclusions

It is shown that the combination of stable isotope tracers, thin film diffusion couples and secondary neutral mass spectrometry can be successfully used for an experimental study of cation diffusion in complex oxide materials.

Copper self-diffusion has been studied for CuO, $Y_2Cu_2O_5$ and $YBa_2Cu_3O_{7-x}$ ceramic samples. The lowest diffusion rate and highest values of the intercept and activation energy were found for the $Y_2Cu_2O_5$ phase.

Self-diffusion in CuO most probably involves a vacancy mechanism, because the non-stoichiometry in this compound is accommodated by vacancies in the cation sublattice exactly as found in NiO, CoO and FeO. This assumption was confirmed by low values of the activation energy and the intercept.

The anisotropy of copper diffusion in $YBa_2Cu_3O_{7-x}$ was found to be in the range 200–400: approximately one order of magnitude smaller than that for Ba and Co. Such a high value for anisotropy of copper self-diffusion may be related to the very high mobility of oxygen vacancies in the Cu(1)—O(1) layer of $YBa_2Cu_3O_{7-x}$ structure.

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