Kinetics and Mechanism of Nd_2CuO_4 Synthesis

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Z. Naturforsch. **49a,** 611–616 (1994); received March 14, 1994

The reaction $Nd_2O_3 + CuO \rightarrow Nd_2CuO_4$ was investigated on the basis of the Wagner-Schmalzried theory of diffusion-driven reactions between crystalline solids, with the help of monodimensional chemical diffusion measurements. It was found that the kinetics of the process is governed by Cu^{2+} diffusion, and the chemical diffusion coefficient $\tilde{D}(Cu^{2+})$ in the Nd_2CuO_4 matrix was obtained ($9.9 \cdot 10^{-13}$, $1.97 \cdot 10^{-12}$ and $1.98 \cdot 10^{-11}$ cm^2 s^{-1} at 1223, 1273 and 1323 K, respectively). The relatively low value of $\tilde{D}(Cu^{2+})$ was interpreted on the basis of the crystal structures of the compound and related materials, which in addition may suggest an alternative rationale for the interpretation of neodymium immobility.

Key words: Nd_2CuO_4 superconductor, Synthesis, Reaction mechanism, Kinetics, Chemical diffusion.

1. Introduction

As found by Tokura et al. [1] in 1989, Ce doped Nd_2CuO_4 is a superconductor with a critical temperature not much above 20 K. The $Nd_{2-x}Ce_xCuO_4$ solid solutions were then believed to be *n*-type conductors, but so far no general agreement is attained about the electronic structure and transport properties of these materials [2–4]. Very broadly speaking, the electronic properties of superconducting oxides at low temperatures can dramatically change depending on the conditions used in the preparation, which is usually carried out through the sequence: i) solid state reaction, ii) sintering and iii) annealing. However, little efforts have been made until now to understand the elementary mechanisms of the solid state synthesis of superconducting oxides.

As a part of a research program devoted to these aspects [5–8], here we present a kinetic study on the formation of Nd_2CuO_4 from Nd_2O_3 and CuO.

From a chemical point of view, this system seems to be ideal for the application of the current Wagner-Schmalzried theory of diffusion-driven reactions between crystalline solids [9] for the following main reasons: i) the compound has a relatively simple tetragonal crystal structure [1], copper and neodymium atoms occupy equivalent positions, whilst only two distinct positions exist for oxygens: as all the atoms are in special positions, we are left with a very small number of positional degrees of freedom in describing the content of the unit cell; ii) data concerning the free energy of formation [10], and the diffusivities of some ionic species [11] are available in the current literature, iii) Nd_2CuO_4 represents a true ternary system, so that only three independent diffusion coefficients exist [12].

2. Experimental

CuO (Aldrich 99.99%) and Nd_2O_3 (Aldrich 99.9%) were used as supplied or sintered at 1173 and 1773 K, respectively, in reagent grade oxygen flux (2 l/h) at $1 \cdot 10^5$ Pa. The monodimensional diffusion couple measurements were performed in a horizontal tube furnace under isothermal (± 1 K) conditions, under a flux (2 l/h) of reagent grade oxygen (or, as indicated in the text, nitrogen) at $1 \cdot 10^5$ Pa, on couples of sintered pellets (8 mm wide, ~ 1.5 mm thick, obtained by pressing uniaxially the powders of the reagents at 10^3 kg cm^{-2}). The experimental apparatus and procedure were previously described [8].

A TA Instruments Thermal Analyst 2000, equipped with an attachment for differential thermal analysis (DTA) from Du Pont were used for thermo-analytic characterisations; alumina crucibles were used as sample holders, with a scan rate of, usually, 5 K min^{-1}.

X-ray Powder Diffraction (XRPD) patterns were taken on a Philips 1710 diffractometer equipped with a copper anode operating at 45 KV and 35 mA, adjustable divergence slit, graphite monochromator on the diffracted beam, and proportional detector. For

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further details on the lattice constant determination procedure, reference is made to a previous paper [8], and to the citations therein.

Optical microscopic observations were made with a Zeiss Axioplan microscope, on couples reacted for a certain time *t*, and then included in epoxy resin (Struers), cut along a plane parallel to the diffusion direction, and polished to optical quality.

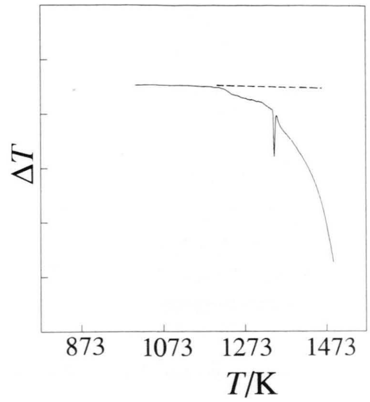

Fig. 1. Differential thermal analysis (DTA) trace for an equimolar mixture of Nd_2O_3 and CuO. The deviation of the base line indicates the beginning of the solid state reaction.

3. Results

For an equimolar mixture of CuO and Nd_2O_3, the DTA trace (see Fig. 1) shows that the reaction starts at 1223 K; the endothermic peak at 1343 K has been ascribed to the eutectic between Nd_2CuO_4 and CuO, in agreement with the equilibrium phase diagram [13]. Accordingly, the diffusion couples method has been applied at three different temperatures, 1223, 1273 and 1323 K, in a pure oxygen flux. In every case, after a suitable reaction time, a single black reaction layer is generally obtained, on the Nd_2O_3 side (Figure 2). The assignment of the layer to Nd_2CuO_4 was performed by XRPD: the lattice constants determination gave $a = b = 0.394382(84)$, $c = 1.21739(26)$ nm.

As an example, in Fig. 3 the data obtained at 1223 K are reported. The (practical) kinetic constants $\bar{k}$ were obtained by measuring the thickness Δx of the product layer at different reaction times, *t*, through the equation: $\Delta x^2 = 2\bar{k}t$. The values are summarised in Table 1. An activation energy of the reaction of 401 kJ mol^{-1} was estimated by Arrhenius plot.

For the sake of completeness, however, thin layer formation also without contact between pellets must be mentioned: this was probably due to a slow copper

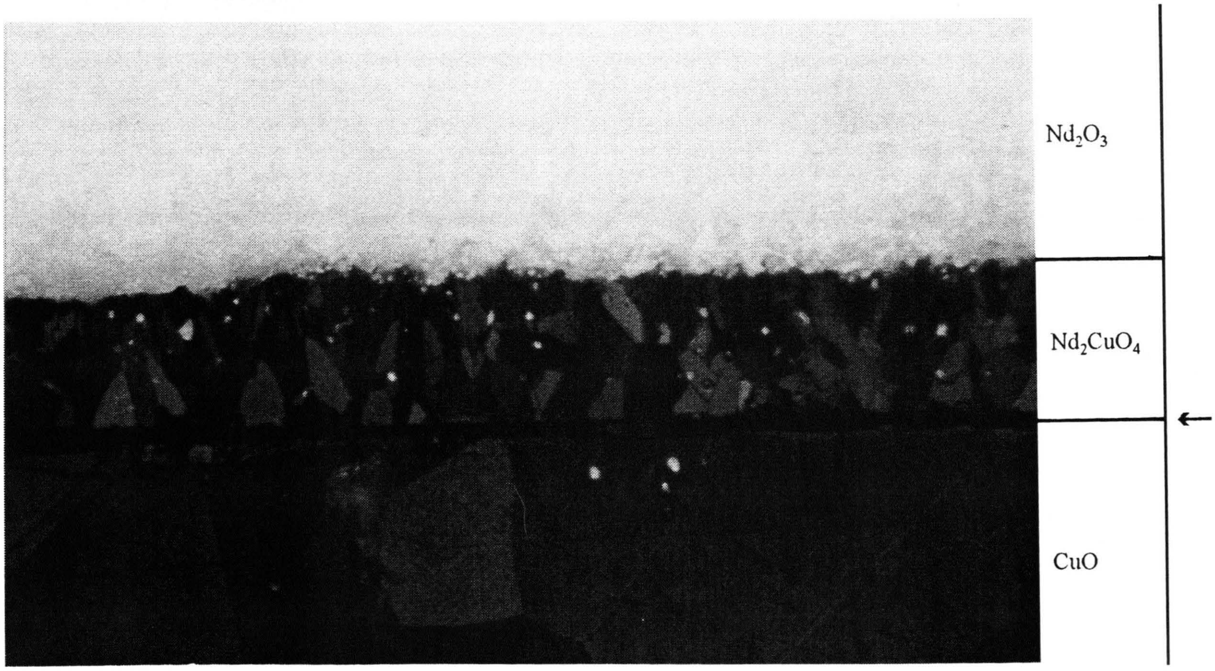

Fig. 2. Scheme and optical micrography of a Nd_2O_3–CuO couple; the arrow indicates the original position of the reaction interface.

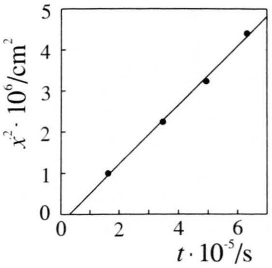

Fig. 3. Monodimensional diffusion for the reaction between the Nd_2O_3 and CuO pellets at 1223 K and $P(O_2) = 10^5$ Pa. Abscissa: reaction time; ordinate: squared thickness of the reaction layer.

Table 1. Relevant kinetic ($\bar{k}$), thermodyamic (ΔG°) and transport ($\tilde{D}$) data for the Nd_2CuO_4 synthesis.

T (K)	$\bar{k}$ ($cm^2\ s^{-1}$)	$\Delta G^\circ (Nd_2CuO_4)$ ($kJ\ mol^{-1}$)	$\tilde{D}(Cu^{2+})$ ($cm^2\ s^{-1}$)
1223	$3.59 \cdot 10^{-12}$	-19.18	$9.9 \cdot 10^{-13}$
1273	$7.32 \cdot 10^{-12}$	-19.63	$1.97 \cdot 10^{-12}$
1323	$7.24 \cdot 10^{-11}$	-20.09	$1.98 \cdot 10^{-11}$

oxide evaporation, which could give a small but effective activity of Cu in the gas phase.

To gain a deeper understanding of the reaction mechanism (see the discussion), diffusion experiments were performed at 1273 K also in pure nitrogen flux: in these conditions, the actual reaction occurs between Nd_2O_3 and Cu_2O. In any case, no significant variation in the product layer thickness was found.

4. Discussion

As previously mentioned, in a ternary system there are only three independent diffusion coefficients [12]; let us denote them with $D(a)$, $D(b)$, and $D(c)$, and suppose, without any loss of generality that

$$D(a) > D(b) > D(c). \tag{1}$$

In the Wagner-Schmalzried theory of solid state reactions in ternary systems [9], the kinetics of the chemical process is determined by the transport of the intermediate diffusivity constituent (b), since the constituent with the smallest diffusion coefficient (c) can be taken as immobile because of the second inequality in (1), and the fastest diffusing constituent (a) is coupled by a local electroneutrality condition with the intermediate one (b).

From the position of the reaction layer with respect to the original reaction interface one can argue that in this case neodymium is immobile; nevertheless, for the reasons explained below, the explicit identification $c \equiv Nd^{3+}$ is not performed, and it is only observed that the reaction mechanism involves the concurrent diffusion of oxygen and Cu^{2+}. In the literature [11] the O^{2-} ion is reported to have a very high chemical diffusion coefficient in the Nd_2CuO_4 matrix (of the order of $10^{-5}\ cm^2\ s^{-1}$ at 1173 K). Moreover, by the experimental finding that a couple reacted at 1273 K in a pure nitrogen flux shows no variation in the layer thickness, one can exclude gas phase transport of oxygen. Thus the rate determining constituent, if attention is given to the very small values of the practical kinetic constants (see Table 1), is to be identified with Cu^{2+}.

The local electroneutrality condition implies the equality of the fluxes (j) of copper and oxide ions,

$$j(Cu^{2+}) = j(O^{2-}), \tag{2}$$

and, according to the theory [9], the practical rate constant becomes

$$\bar{k} = -\frac{2\tilde{D}(Cu^{2+})}{RT} \Delta G^\circ (Nd_2CuO_4), \tag{3}$$

where $\Delta G^\circ (Nd_2CuO_4)$ is the standard Gibbs free energy variation associated with the reaction, which can be obtained from literature data*: thus the chemical diffusion coefficient of the copper ion $\tilde{D}(Cu^{2+})$ was evaluated from the kinetic determinations. The results are summarised in Table 1: the activation energy of diffusion could be estimated as 400 kJ mol^{-1}.

At this point two remarks must be made. The first one concerns the reliability of the diffusion coefficient(s) determination: unfortunately, literature data on the diffusivity of Cu^{2+} in neodymium cuprate are, until now, not available, so that the validity of this approach cannot be directly checked. Nevertheless, a useful even if indirect estimate of these results can be

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* According to the data by Petrov et al. [10] for the reactions

$$2\,NdCuO_2 + Nd_2O_3 + 1/2\,O_2 \rightarrow 2\,Nd_2CuO_4, \quad \Delta G^\circ(1),$$

$$4\,NdCuO_2 + 1/2\,O_2 \rightarrow 2\,Nd_2CuO_4 + Cu_2O, \quad \Delta G^\circ(2)$$

and by Jacob et al. [14] for the reaction

$$2\,Cu_2O + O_2 \rightarrow 4\,CuO, \quad \Delta G^\circ(3)$$

it follows that

$$\Delta G^\circ (Nd_2CuO_4) = 1/2\,\{[2\,\Delta G^\circ(1) - \Delta G^\circ(2)] - 1/2\,\Delta G^\circ(3)\}.$$

obtained by comparing the $\tilde{D}(Cu^{2+})$ so obtained with the self-diffusion coefficient $D^*(Cu^{2+})$ in YBCO superconductor [15], namely a compound in which the chemical environment of copper is very similar to that of Nd_2CuO_4**. Figure 4 compares the Arrhenius plots for the two diffusion coefficients, together with the same plot for the chemical diffusion coefficient of the oxide ion in Nd_2CuO_4 [11]. It is readily seen that copper diffusion, at a given temperature, is easier in YBCO than in neodymium cuprate. In structural terms, this is nicely explained taking into account the coordination of copper in the two unit cells (see Figure 5). As in Nd_2CuO_4 the oxygen non-stoichiometry is not very important, almost every copper atom is in a square planar coordination; in the orthorhombic $YBa_2Cu_3O_{7-x}$, even if $x = 0$, the O_1 site is only half occupied; moreover, this compound is heavily non-stoichiometric, and when $x = 1$, every O_1 is empty, the cell symmetry becomes tetragonal, and YBCO undergoes a phase transition. It is clear that an oxygen vacancy in the O_1 site lowers the coordination number of two copper atoms: therefore, even if only steric hindrance is taken into account, a greater diffusivity of copper in YBCO than in Nd_2CuO_4 is easily expected.

The second remark regards the influence on the reaction mechanisms of the structural relationships between the product and the parent materials. When dealing with a solid state reaction, as long as the kinetics can be considered diffusion limited, only the transport properties (i.e. the proper diffusion coefficients) of the product are usually taken into consideration. Although this approach is quite reasonable, it must be pointed out that for a given negligible flux there may be: i) a negligible diffusion coefficient and/or ii) *a negligible chemical potential gradient.*

Consequently, it can be inferred that the immobility of neodymium may admit another explanation, *external to the Wagner-Schmalzried theory*, if the structures of neodymium cuprate [1] and hexagonal neodymium oxide [17] (which is stable at the reaction temperature [18]) are taken into account. For this purpose it is necessary to consider only the neodymium sub-lattices (Fig. 6), which are easily seen as different modifications of the neodymium sub-lattice of an ideal $Nd(O, V_O)_2$ fluorite structure (note that the cubic Nd_2O_3, stable at low temperature [18], has the latter structure, also shown in Figure 6). In the fluorite structure (space group Fm3m), along a ⟨001⟩ direction, two different neodymium planes are found,

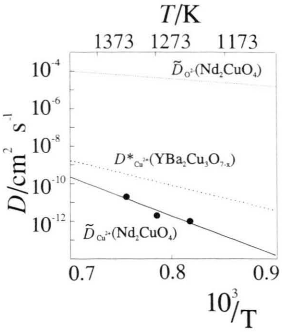

Fig. 4. Arrhenius plot of the chemical diffusion coefficient of Cu^{2+} in Nd_2CuO_4 and of the self-diffusion coefficient of Cu^{2+} in YBCO; the chemical diffusion coefficient of O^{2-} in Nd_2CuO_4 is also plotted.

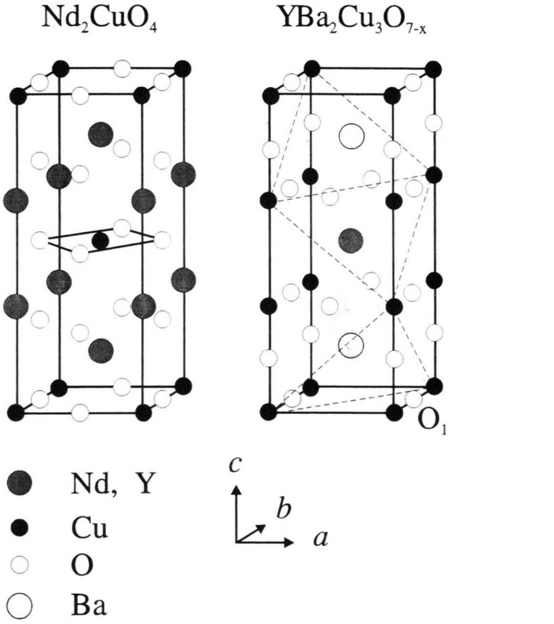

Fig. 5. Comparison of the unit cells of Nd_2CuO_4 (left) and $YBa_2Cu_3O_{7-x}$ (right). The dashed lines within the YBCO cell refer to the ⟨110⟩, ⟨301⟩ and ⟨031⟩ directions, proposed by Jorgensen et al. [16] as preferential jump directions for Cu^{2+}.

** It must be noted that two different quantities are being compared, i.e. a chemical diffusion coefficient and a self-diffusion coefficient, which are related by

$$\tilde{D}_i = D_i^* \left(\frac{\partial \ln a_i}{\partial \ln c_i} \right),$$

so that they are equal only in the limit of ideal defects behaviour. This assumption is here reasonably justified, since we are far enough from the melting point.

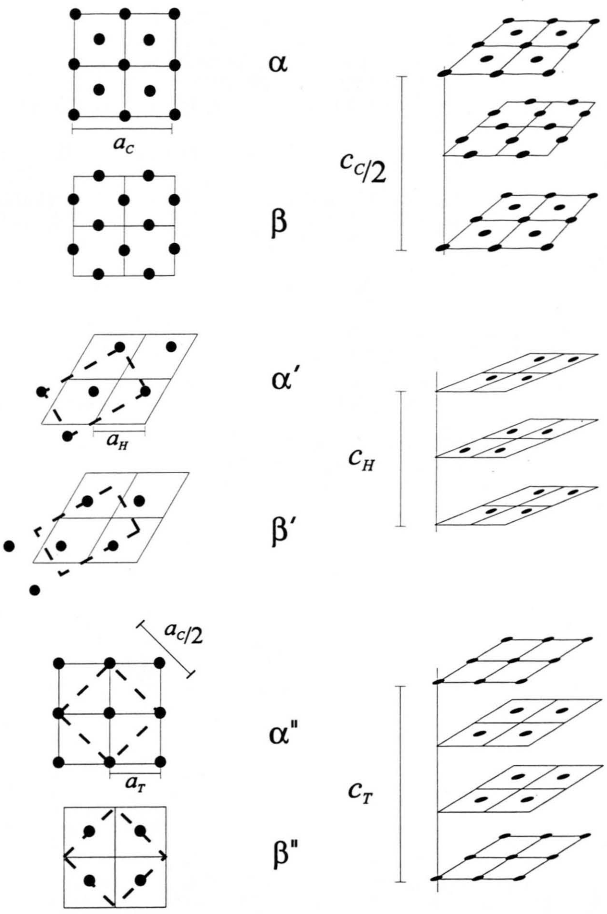

Fig. 6. Neodymium sub-lattices in cubic Nd_2O_3 (upper part), in hexagonal Nd_2O_3 (middle part), and in neodymium cuprate (lower part); the dashed lines represent the related fluorite network. The stacking sequence for the three structures is also shown. For the meaning of the symbols in this figure see the text.

marked with α and β in Figure 6: the stacking sequence is αβαβαβαβ .... In the hexagonal neodymium oxide (space group P$\bar{3}$m1 ***), along the ⟨001⟩ direction the same planes are found (α′ and β′ in Fig. 6), with the same stacking sequence α′β′α′β′α′β′α′β′..., a rectangular deformation and a small shifting in the β′ planes. Finally, also in Nd_2CuO_4 (space group I4/mmm) along the ⟨001⟩ direction Nd atoms build up the same fluorite-like planes (α″ and β″ in Fig. 6) with a stacking sequence α″β″β″α″α″β″β″α″...; as clues, the facts may be quoted that: i) the a_T ($a_T = 0.3944$ nm [21]) constant of Nd_2CuO_4 is almost exactly $\frac{\sqrt{2}}{4}$ times the a_C constant of the cubic Nd_2O_3 $\left(a_C = 1.108 \text{ nm [22]}, \frac{\sqrt{2}}{4} \cdot a_C = 0.3917 \text{ nm}\right)$, ii) the a_T constant of Nd_2CuO_4 is almost equal to the a_H ($a_H = 0.3831$ nm [23]) constant of the hexagonal Nd_2O_3.

As an incidental observation, the conversion of the hexagonal neodymium oxide into the neodymium cuprate can be seen as the occurrence of i) some small rearrangement of the neodynium and oxygen setting up, ii) filling up of all the oxygen vacancies, and iii) insertion of copper ions in some interstitial sites.

These structural relationships suggest that the activity of neodymium does not change remarkably in the three structures. Moreover, the concentration of neodymium, measured in atoms per unit volume, is practically the same: $2.4 \cdot 10^{-5}$ nm^{-3} in cubic neodymium oxide, $2.6 \cdot 10^{-5}$ nm^{-3} in hexagonal neodymium oxide and $2.2 \cdot 10^{-5}$ nm^{-3} in neodymium cuprate. Therefore it is not unreasonable to suppose that, both at the Nd_2O_3–Nd_2CuO_4 interface and in the whole reaction layer, the neodymium chemical potential gradient is negligible. Thus the neodymium flow might be near zero, neglecting the actual value of the neodymium diffusion coefficient. It is here perhaps worth noting that, in the YBCO superconductor, above 1200 K, the self-diffusion coefficient of yttrium (which has a chemical environment very similar to that of neodymium in Nd_2CuO_4) is at least comparable with the self-diffusion coefficient of copper [15].

Finally the authors wish to point out that they are positively not proposing an atomistic reaction mechanism; in this respect, this is only a tentative interpretation which ought to be experimentally verified, for example reacting properly oriented single crystals.

Acknowledgements

The authors wish to thank Profs. G. Flor and G. Spinolo for helpful discussions and careful reading of the manuscript.

*** For the sake of semplicity, use was here made of an approximated structural model proposed by L. Pauling [17]; this model was revised in some details by Müller-Buschbaum et al. [19, 20], who attributed the structure to a different space group (P6_3/mmm).

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