

Short Communication

Superconducting Cuprates and Related Oxides. IX. *In Situ* Synchrotron X-Ray Powder Diffraction Investigation of the Oxidation and Reduction of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in a Flow of Oxygen or of Nitrogen Gas in the Temperature Range 400–725 °C

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The formation of tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in a solid-state reaction process from a mixture of yttrium oxide, copper oxide and barium carbonate is achieved within 3–6 h at a temperature of 950 °C.¹ The oxidation of the tetragonal to the orthorhombic superconducting compound is in general assumed to be a rather slow gas–solid reaction, and the oxidation takes at least several days for larger single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. It would be of interest to know how fast this gas–solid reaction proceeds in the temperature range 400–550 °C, in which range orthorhombic superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ traditionally is obtained by annealing in a flow of oxygen gas. For this reason, an *in situ* synchrotron X-ray powder diffraction investigation of the oxidation and reduction of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in a flow of O_2 or N_2 gas has been investigated.

Experimental

The sample of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ used was made from the starting materials Y_2O_3 (Auer-Remy, 99.99%), BaO (Merck p.a.) and CuO (Merck p.a.). These were weighed out to give a 15 g reaction mixture and mixed in a porcelain mortar, pressed into 25 mm diameter pellets and heated in a muffle furnace at 950 °C for 12 h. The pellets were reground, pressed into new pellets and heated

in a tube furnace in an oxygen gas flow at 950 °C for 24 h followed by 550 °C for 12 h. The sample of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ so obtained showed the Meissner effect when cooled in liquid nitrogen, and the X-ray powder pattern of the sample recorded with a Stoe-Stadi powder diffractometer showed that it was orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The pellets were reground and sieved through a 0.12 mm sieve.

Standard reference samples of orthorhombic and tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ were made by heating powder samples of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in a tube furnace in a flow of O_2 or N_2 , respectively, as indicated in Table 1, and the phases so obtained were identified from their X-ray powder patterns measured with the Stoe–Stadi

Table 1. Experimental conditions for annealing of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in O_2 or N_2 gas, respectively.

| No. | | Powder pattern | JCPDS No. |
|---|-------------------|---|-----------|
| Annealing in O_2 gas at 725 °C for 15 min followed by: | | | |
| A | 400 °C for 20 h | $\text{YBa}_2\text{Cu}_3\text{O}_{6.8}$ | 39-486 |
| B | 475 °C for 20 h | $\text{YBa}_2\text{Cu}_3\text{O}_{6.8}$ | 39-486 |
| C | 550 °C for 20 h | $\text{YBa}_2\text{Cu}_3\text{O}_{6.8}$ | 39-486 |
| Annealing in N_2 gas: | | | |
| D | 400 °C for 13 h | $\text{YBa}_2\text{Cu}_3\text{O}_{6.8}$ | 39-486 |
| E | 475 °C for 14 h | $\text{YBa}_2\text{Cu}_3\text{O}_6$ | 39-1496 |
| F | 550 °C for 13 h | $\text{YBa}_2\text{Cu}_3\text{O}_6$ | 39-1496 |
| G | 725 °C for 0.25 h | $\text{YBa}_2\text{Cu}_3\text{O}_6$ | 39-1496 |

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powder diffractometer. No chemical analyses of the oxygen content were made. At 400 °C the orthorhombic compound was not converted to the tetragonal compound by annealing in N₂ gas, which, however, was the case when the annealing took place at the temperatures 475, 550 and 725 °C, respectively.

The samples of YBa₂Cu₃O_{7-δ} used for the *in situ* investigations were housed in 0.5 mm diameter quartz capillaries, mounted on a goniometer so that a gas flow through the capillaries could be realized. The nitrogen gas used was 99.99% N₂ and the oxygen gas used was a gas mixture of 90% O₂ and 10% N₂. The synchrotron X-ray powder patterns were measured on a Huber diffractometer at the beam line X7B at NSLS, Brookhaven National Laboratory. The detector used was a moving imaging plate system built for time-, temperature- and wavelength-dependent powder diffraction.² The *in situ* measurements were made with (i) an oxygen or nitrogen gas flow in the capillaries and temperature heating range from 30 to 725 °C or from 30 to 550 °C, or (ii) isothermal at fixed temperatures between 400 and 725 °C with an oxygen gas flow, followed by a nitrogen gas flow, or *vice versa*. The gas flow in the capillaries was ca. 10 l/h and could easily be shifted from oxygen to nitrogen within 10 s. The experimental conditions for the *in situ* measurements are listed in Table 2.

Discussion

The *in situ* experiments were performed (i) in a temperature range and (ii) isothermal. The results obtained are

as follows (Table 2). (The experiments listed in the table are referred to below as numbers in parenthesis.)

(i) *Measurements in a heating range.* Orthorhombic YBa₂Cu₃O_{7-δ} transforms to the tetragonal compound when heated in air (1) at a heating rate of 11.5 °C min⁻¹, and also when heated in a flow of N₂ (2) at a heating rate of 5.8 °C min⁻¹. Tetragonal YBa₂Cu₃O_{7-δ} transforms to the orthorhombic compound (3) when heated in a flow of O₂ at a heating rate of 5.8 °C min⁻¹. The tetragonal and orthorhombic compounds are stable when heated in a flow of N₂ or O₂, respectively, (4) and (5).

(ii) *Isothermal measurements in flow of O₂ or of N₂.* The isothermal measurements (6)–(19) were all made with the same sample. The starting composition, orthorhombic or tetragonal compound, was achieved when necessary by oxidation or reduction in a flow of O₂ or N₂ gas, respectively, at 550 °C. Orthorhombic YBa₂Cu₃O_{7-δ} was not reduced in a flow of N₂ gas at 400 °C (6) and at 425 °C (8), but tetragonal YBa₂Cu₃O_{7-δ} was oxidized in a flow of O₂ gas at 400 °C (7) and at 425 °C (9). At all the other temperatures investigated, 450, 475, 500, 550 and 725 °C, it was observed that the phase transitions of tetragonal YBa₂Cu₃O_{7-δ} to orthorhombic YBa₂Cu₃O_{7-δ} in a flow of O₂ gas, (11), (13), (15), (17), (19), and the phase transitions of orthorhombic to tetragonal YBa₂Cu₃O_{7-δ} in a flow of N₂ gas, (10), (12), (14), (16), (18) proceeded immediately after the change of gas flow. Information on the imaging plates is converted into a series of powder patterns which are displayed so they

Table 2. Experimental conditions for *in situ* measurements of phase transitions of YBa₂Cu₃O_{7-δ} in oxygen or nitrogen gas flow. Orthorhombic YBa₂Cu₃O_{6.8}(O), tetragonal YBa₂Cu₃O₆(T).

| (i) measurements in a heating range: | | | | | | |
|---|-------------------|-------------------------|---|---|------------------|----------------|
| No. | Starting material | T _{min} /°C | T _{max} /°C | Heating rate /°C min ⁻¹ | Phase transition | Gas flow |
| (i) measurements in a heating range: | | | | | | |
| 1 | O | 30 | 725 | 11.5 | O→T | None |
| 2 | O | 30 | 725 | 5.8 | O→T | N ₂ |
| 3 | T | 30 | 550 | 5.8* | T→O | O ₂ |
| 4 | T | 25 | 550 | 4.4 | no transition | N ₂ |
| 5 | O | 25 | 550 | 4.4 | no transition | O ₂ |
| x Kept at 600 °C for 6 h | | | | | | |
| (ii) isothermal measurements in flow of O ₂ or of N ₂ : | | | | | | |
| No. | Starting material | T/°C | O ₂ -flow→N ₂ -flow | N ₂ -flow→O ₂ -flow | Phase transition | |
| 6 | O | 400 | + | | None | |
| 7 | T | 400 | | + | T→O | |
| 8 | O | 425 | + | | None | |
| 9 | T | 425 | | + | T→O | |
| 10 | O | 450 | + | | O→T | |
| 11 | T | 450 | | + | T→O | |
| 12 | O | 475 | + | | O→T | |
| 13 | T | 475 | | + | T→O | |
| 14 | O | 500 | + | | O→T | |
| 15 | T | 500 | | + | T→O | |
| 16 | O | 550 | + | | O→T | |
| 17 | T | 550 | | + | T→O | |
| 18 | O | 725 | + | | O→T | |
| 19 | T | 725 | | + | T→O | |

show the evolution in time of the patterns when a phase transition occurs in the sample. Figure 1 shows a section of the powder patterns from the oxidation of tetragonal to orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at 725°C (19). After 4 min the N_2 gas flow was shifted to an O_2 gas flow. A change in the patterns is observed almost immediately. The Bragg reflections at the 2θ values 22.97 and 23.23° in the first 12 diagrams are the 103 and the 110 reflections of tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The reflection at $2\theta = 23.70^\circ$, which is unchanged in the oxidation, is from an impurity. The Bragg reflection at the 2θ value 23.00 and the strong reflection at 23.25 in the following diagrams are the 013 and the 103 reflections of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

Figure 2 shows a section of the powder patterns from an oxidation at 500°C (15). After 2 min the N_2 gas flow was shifted to an O_2 gas flow. Also, at this temperature a change in the patterns is observed almost immediately. The Bragg reflection at $2\theta = 40.50^\circ$ in the first 20 patterns is the 213 reflection of tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, and the

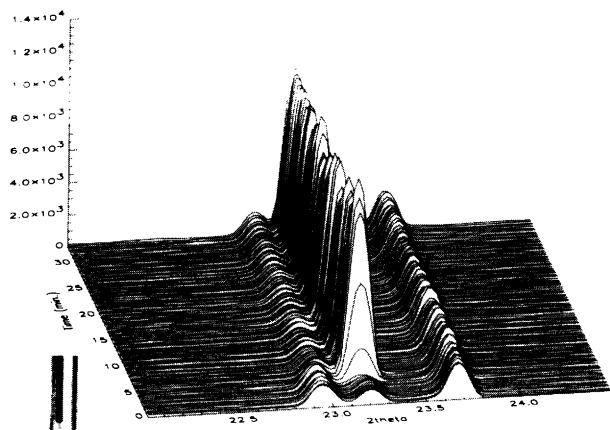


Fig. 1. Patterns of yttrium barium cuprate showing the transformation of tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ to orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in oxidation with O_2 gas at 725°C .

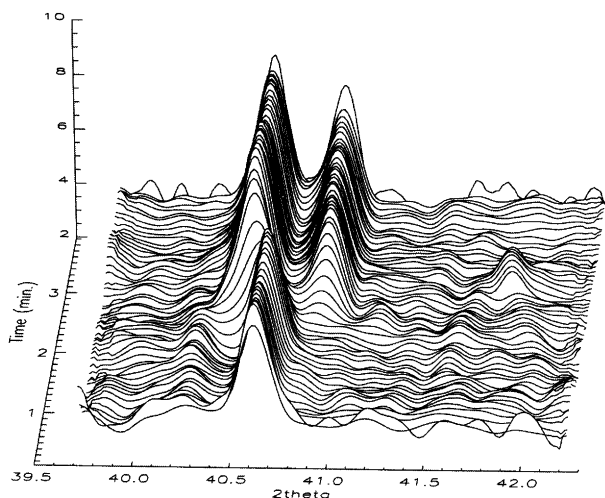


Fig. 2. Patterns of yttrium barium cuprate showing the effects of oxidation with O_2 gas at 500°C in the transformation of tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ to orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

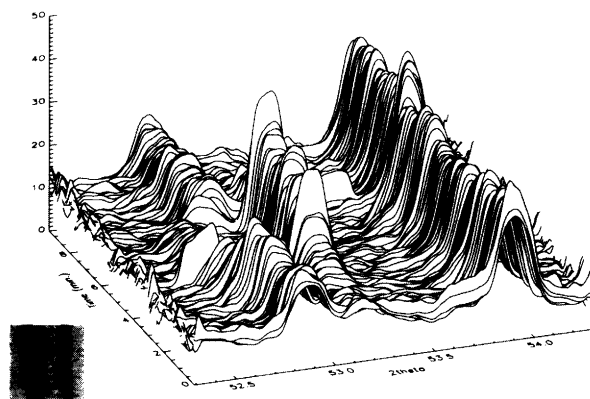


Fig. 3. Patterns of yttrium barium cuprate showing the transformation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ from orthorhombic to tetragonal and back to orthorhombic in treatment with O_2 , N_2 and O_2 gas, respectively, at 450°C .

Bragg reflections at the 2θ values 40.30 and 40.80 in the remaining patterns are the 123 and the 213 reflections of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

Figure 3 displays a section of the powder patterns from oxidation, reduction and oxidation again at 450°C (10) and (11). The O_2 gas flow was after 3 min shifted to an N_2 gas flow, which after additional 3 min was shifted to an O_2 gas flow. The Bragg reflections at the 2θ values 53.00 and 54.20 are the 130 and the 303 reflections of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, and the Bragg reflections at the 2θ values 53.40 and 54.20 are the 303 and the 310 reflections of tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The reduction proceeds somewhat more slowly than the oxidation of the sample at 450°C , but reduction as well as oxidation are, however, fast processes at 450°C . The investigation thus shows that the gas-solid oxidation and reduction processes of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with O_2 and N_2 gas, respectively, are fast processes. The long time periods required for the oxidation of larger single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ to obtain samples which are superconductors at temperatures close to 90 K are thus due to the slow oxygen diffusion processes in the bulk.

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References

1. Conroy, L. E., Christensen, A. N. and Böttiger, J. *Acta Chem. Scand., Ser. A41* (1987) 501.
2. Norby, P. *Mater. Sci. Forum. In press.*

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