## Short Communication

# Superconducting Cuprates and Related Oxides X. *In-Situ* Neutron Powder Diffraction Investigation of the Solid State Synthesis of $YBa_2Cu_3O_{7-\delta}$ in a Flow of Oxygen at Temperatures up to 950 °C

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The tetragonal cuprate, $YBa_2Cu_3O_{7-\delta}$, which is the precursor phase for the orthorhombic high-$T_c$ superconductor $YBa_2Cu_3O_{7-\delta}$, can be obtained at 950 °C in a solid-state reaction from a $Y_2O_3$–$BaCO_3$–$CuO$ mixture. In a previous investigation it was demonstrated that the reaction at 950 °C is complete within 4 h, and that the compound $BaY_2CuO_5$ was formed as an intermediate phase.[1] Barium oxide reacts more readily than barium carbonate in solid state reactions. In a preliminary investigation using a $Y_2O_3$–$BaO$–$CuO$ mixture at the reaction temperatures 800 and 900 °C it was found that the formation of the cuprate went through formation of the precursor phase $BaCuO_2$, and that this phase was formed within 20 min. Pellets of the mixture of $Y_2O_3$–$BaO$–$CuO$ were placed in a furnace at 800 or 900 °C at time periods from 20 min to 3.5 h. After the heat treatment, qualitative phase analysis of the pellets was made based on X-ray powder diffraction. However, a more detailed information on the solid-state sintering processes may be obtained by *in-situ* powder diffraction, and for this reason investigation of the sintering reaction was made in an *in-situ* neutron powder diffraction investigation.

## Experimental

The investigation was made using the neutron powder diffractometer E2 at the Hahn–Meitner Institute in Berlin using a neutron wavelength of 2.406 Å. The flux at the sample position of E2 is $2 \times 10^6$ $n/cm^2$ s.

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A stoichiometric reaction mixture was made of $Y_2O_3$ (Auer-Remy), BaO (Alfa) and CuO (Merck). The reaction mixture was placed in a quartz glass tube under an oxygen flow of 0.15 L $min^{-1}$. The tube was heated in a vacuum furnace controlled by an ILL precision temperature controller. Four *in-situ* experiments were performed with the temperature ramped to the temperatures listed in Table 1, where the heating rates are also listed. The samples were kept at the reaction temperatures for sufficient time for the chemical reactions to reach equilibrium. Almost all chemical reactions took place when the temperature was ramped, and only marginal changes were observed in the powder patterns recorded at the constant temperatures.

The phases formed in the *in-situ* investigations were identified from the neutron diffraction powder patterns. Theoretical neutron diffraction powder patterns were calculated using the program LAZY PULVERIX,[2] and the structural information for the compounds listed in Table 2.

## Results

The results of the investigation are that BaO and CuO reacts faster than $Y_2O_3$. Two precursor phases are formed. $Ba_2Cu_3O_{5+\delta}$, whose formation starts as low as at 350 °C, starts to decompose above 800 °C, forming the second precursor phase $BaCuO_2$ and CuO, and $BaCuO_2$ reacts finally to produce tetragonal $YBa_2Cu_3O_{7-\delta}$. Figures 1–4 show patterns from experiment No. 1. Figure 1 shows the neutron diffraction powder pattern

*Table 1.* Experimental conditions for the *in-situ* investigation and crystalline phases identified.

| Experiment no. | Heating rate/$^\circ$C h$^{-1}$ | $T_{max}/^\circ$C | Time at $T_{max}$/h | Intermediate phases observed | Reaction products | |
|---|---|---|---|---|---|---|
| | | | | | Impurity | Main product |
| 1 | 567 | 950 | 2 | $Ba_2Cu_3O_{5+\delta}$, $BaCuO_2$ | | $YBa_2Cu_3O_{7-\delta}$ |
| 2 | 280 | 900 | 5.5 | $Ba_2Cu_3O_{5+\delta}$, $BaCuO_2$ | $BaCuO_2$ | $YBa_2Cu_3O_{7-\delta}$ |
| 3 | 130 | 850 | 2.5 | $Ba_2Cu_3O_{5+\delta}$, $BaCuO_2$ | $BaCuO_2$ | $YBa_2Cu_3O_{7-\delta}$ |
| 4 | 467 | 800 | 7 | $Ba_2Cu_3O_{5+\delta}$ | | $Ba_2Cu_3O_{5+\delta}$ |

*Table 2.* List of reactants and possible reaction products with reference to X-ray powder patterns and crystal structures.

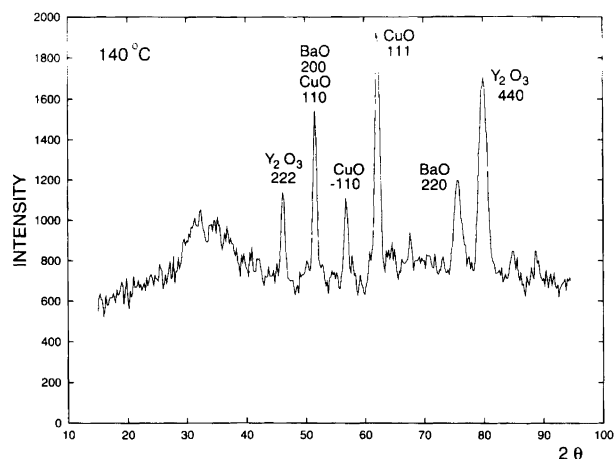| Compound | JCPDS card no. | Ref. to structure |
|---|---|---|
| BaO | 21–1056 | 3 |
| CuO | 41–254 | 4 |
| $Y_2O_3$ | 43–1036 | 5 |
| $Ba_2Cu_3O_{5+\delta}$ | 40–762 | 6 |
| $BaCuO_2$ | 38–1402 | 7 |
| $BaY_2CuO_5$ | 38–1434 | 8 |
| $YBa_2Cu_3O_6$ | 39–1496 | 9 |
| $YBa_2Cu_3O_7$ | 38–1433 | 10 |



*Fig. 1.* Neutron diffraction powder pattern of the $Y_2O_3$–BaO–CuO reaction mixture recorded at 140 $^\circ$C with 2.406 Å neutrons.



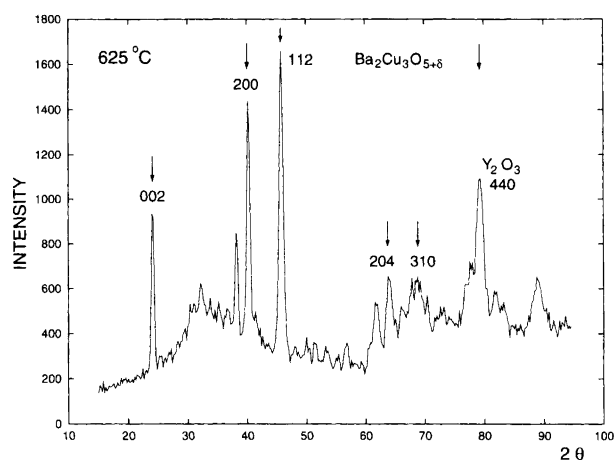*Fig. 2.* Neutron diffraction powder pattern recorded at 625 $^\circ$C showing Bragg reflections of $Ba_2Cu_3O_{5+\delta}$ and $Y_2O_3$.
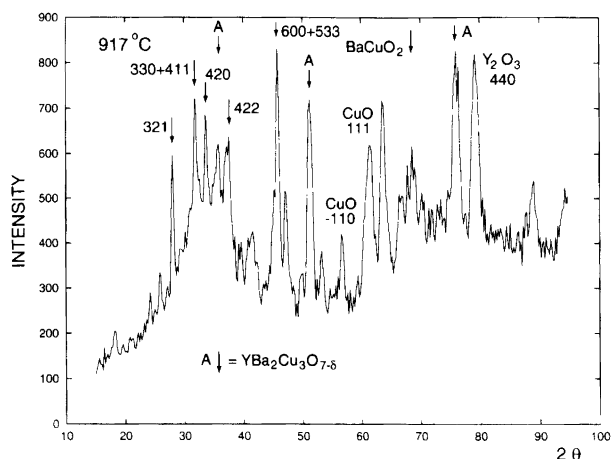


*Fig. 3.* Neutron diffraction powder patterns recorded at 917 $^\circ$C showing Bragg reflections of $BaCuO_2$, CuO and of $Y_2O_3$.
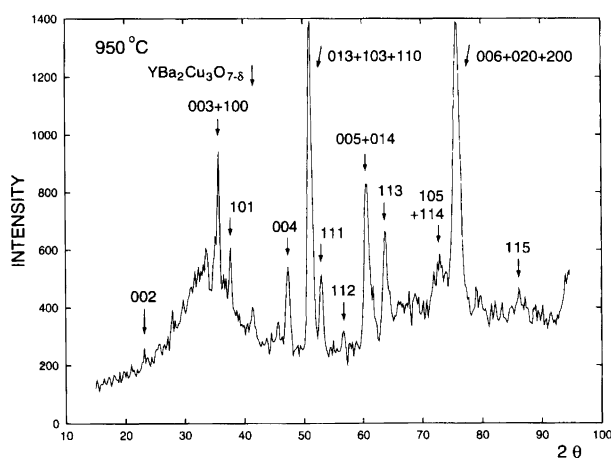


*Fig. 4.* Neutron diffraction powder patterns recorded at 950 $^\circ$C showing Bragg reflections of $YBa_2Cu_3O_{7-\delta}$.

of the reaction mixture at 140 $^\circ$C. The high background in the $2\theta$ interval 30–40$^\circ$ is the scattering contribution from the quartz glass tube. Figure 2 shows the powder pattern of the sample taken at 625 $^\circ$C. The Bragg reflections from $Y_2O_3$ are still present, the reflections of BaO and CuO are absent, and the pattern shows reflections of $Ba_2Cu_3O_{5+\delta}$. Figure 3 shows the powder pattern of the reaction mixture at 917 $^\circ$C. The reflections of $Y_2O_3$ are still present, but $Ba_2Cu_3O_{5+\delta}$ is almost completely converted to $BaCuO_2$ and CuO. Finally, Figure 4 shows the Bragg reflections of the reaction

product, tetragonal $YBa_2Cu_3O_{7-\delta}$. Figure 5 is a plot of selected Bragg intensities vs. temperature and time for experiment No. 1. It shows that $BaCuO_2$ is only present in a short temperature interval between approximately 800–950 °C. Figure 6 is a display of selected Bragg reflection intensities vs. temperature and time for experiment No. 4, where the maximum temperature was 800 °C. The precursor phase $Ba_2Cu_3O_{5+\delta}$ is present throughout the time period in which the sample is kept at 800 °C. Figure 7 shows a stack of powder patterns from experiment No. 1.

The *in-situ* investigation of the solid state synthesis of tetragonal $YBa_2Cu_3O_{7-\delta}$ from a stoichiometric mixture of $Y_2O_3$–BaO–CuO shows that two intermediate compounds are formed during the heating of the mixture, $Ba_2Cu_3O_{5+\delta}$ and $BaCuO_2$, before $YBa_2Cu_3O_{7-\delta}$ is formed at 950 °C. The reaction temperatures 800, 850
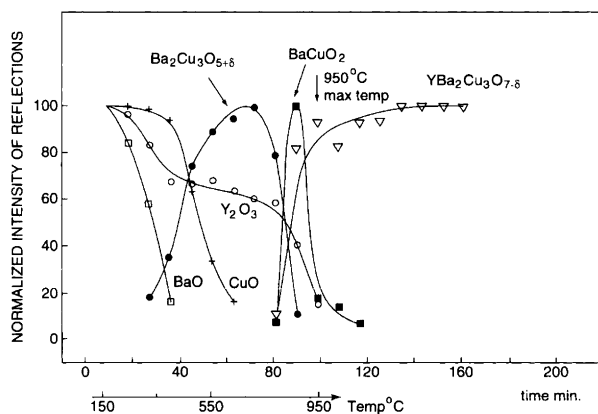
*Fig. 7.* Stack of neutron diffraction powder patterns showing how the reaction mixture of $Y_2O_3$–BaO–CuO is converted to $YBa_2Cu_3O_{7-\delta}$. Nos. 1, 2, 3, and 4 refer to Figs. 1, 2, 3 and 4, respectively.

and 900 °C are not sufficiently high to ensure the formation of tetragonal $YBa_2Cu_3O_{7-\delta}$ as a pure phase within the time used in the investigation (Table 1). The green compound $BaY_2CuO_5$, which was observed as an intermediate phase in a previous investigation[1] using mixtures of $Y_2O_3$–$BaCO_3$–CuO, was not observed in this investigation.

*Fig. 5.* Intensities of selected Bragg reflections of BaO, CuO, $Y_2O_3$, $Ba_2Cu_3O_{5+\delta}$, $BaCuO_2$, and $YBa_2Cu_3O_{7-\delta}$ vs. time and temperature. The precursor phase $Ba_2Cu_3O_{5+\delta}$ is completely consumed before the maximum temperature 950 °C is reached; the precursor phase $BaCuO_2$ is almost completely consumed before 950 °C is reached, and is completely consumed in time at 950 °C.
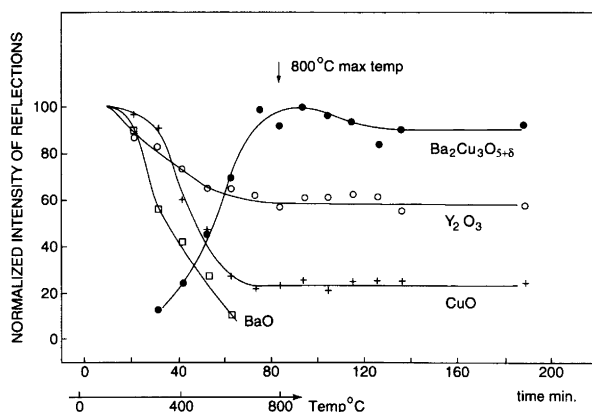
*Fig. 6.* Intensities of selected Bragg reflections of BaO, CuO, $Y_2O_3$ and $Ba_2Cu_3O_{5+\delta}$ vs. time and temperature. BaO is consumed before the maximum temperature 800 °C is reached and $Ba_2Cu_3O_{5+\delta}$ is only slowly consumed in time at 800 °C.

## References

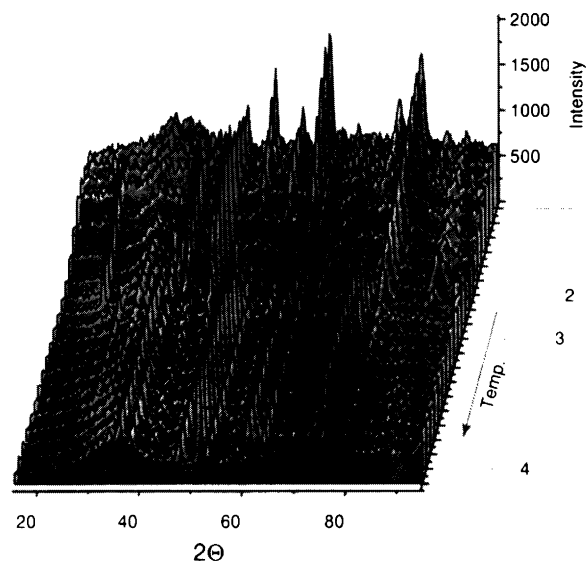1. Conroy, L. E., Christensen, A. N. and Bøttiger, J. *Acta Chem. Scand., Ser. A 41* (1987) 501.
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