

## Superconducting Cuprates and Related Oxides, VI. Crystal Growth of Ternary Cuprates from a BaO–CuO Flux

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Christensen, A. N., 1992. Superconducting Cuprates and Related Oxides, VI. Crystal Growth of Ternary Cuprates from a BaO–CuO Flux. – Acta Chem. Scand. 46: 909–912.

Several research groups (Refs. 1–14) have reported on the crystal growth of the cuprates  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and  $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (RE = lanthanide). It is most common to grow these crystals from a BaO–CuO flux by programmed cooling at temperatures from 1000 to 900 °C. Determinations of phase diagrams of the ternary systems<sup>15–18</sup>  $\text{Y}_2\text{O}_3$ –BaO–CuO and  $\text{RE}_2\text{O}_3$ –BaO–CuO have contributed considerably to the success of these crystal growth experiments.

The tetragonal modifications of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and  $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$  are formed in the flux growth, and the crystals must be annealed in oxygen at 500 °C for several days to be converted into the orthorhombic superconducting forms of the compounds. The crystals grow as thin plates with dimensions up to  $6 \times 6 \times 0.8$  mm<sup>3</sup> for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .<sup>5</sup> These crystals are fairly small compared to the size of crystals of other materials grown from a flux.<sup>19</sup> In spite of the considerable competitions in this research field (Refs. 1–14), it was decided to investigate the growth of some tetragonal ternary cuprates. In a previous publication the syntheses of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and  $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (RE = Pr, Nd, Gd, Ho, Yb) were reported.<sup>20</sup> The present work describes crystal growth experiments of the same cuprates.

### Experimental

The following chemicals were used in the crystal growth experiments:  $\text{BaCO}_3$  (Merck *p.a.*),  $\text{CuO}$  (Merck *p.a.*),  $\text{Y}_2\text{O}_3$  (Fluka, *puriss.*, Auer-Remy 99.99%),  $\text{Pr}_6\text{O}_{11}$  (Auer-Remy 99.9%),  $\text{Nd}_2\text{O}_3$  (Koch-Light, Auer-Remy 99.9%),  $\text{Gd}_2\text{O}_3$  (Fluka, *puriss.*, Auer-Remy 99.9%),  $\text{Ho}_2\text{O}_3$  (Fluka, *puriss.*, Auer-Remy 99.9%),  $\text{Yb}_2\text{O}_3$  (Fluka, *puriss.*, Auer-Remy 99.9%) and  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (Haldor Topsøe A/S).  $\text{REBa}_2\text{Cu}_3\text{O}_7$  was obtained from a previous in-house synthesis of polycrystalline samples.<sup>21</sup>

The quantities of the chemicals used in each crystal growth experiment are listed in Table 1 for the growth of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and in Table 2 for the growth of the  $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$  crystals. The chemicals were mixed care-

fully in a porcelain mortar, placed in crucibles of  $\text{Al}_2\text{O}_3$ , and heated to 850 °C for 12 h. The mixture was then ground in a porcelain mortar and pressed into pellets at a pressure of 400 MPa in a mould of cemented carbide. The pellets had typically a diameter of 25 mm and a thickness of up to 5 mm. A pile of 12–15 pellets was placed in a crucible of  $\text{Al}_2\text{O}_3$  in the crystal growth furnace at room temperature. The  $\text{Al}_2\text{O}_3$  crucibles used were 150 ml crucibles from Holdenwanger, Berlin. The idea of charging the mixture as a pile of pellets in the crucible was chosen to minimize contact between the melt and the inside wall of the crucible. In this way, the upper inside wall of the crucible was not wetted with melt, and in none of the crystal growth experiments was creeping of the melt over the edge of the crucible observed. Such creeping of the flux has been observed previously.<sup>22,23</sup>

The crystal growth furnace was a vertical tube furnace, heated with silicon carbide heating elements and programmed with a Eurotherm unit. The heating/cooling programs of the experiments are indicated in Tables 1 and 2. The  $\text{Al}_2\text{O}_3$  crucible was supported by a tube of  $\text{Al}_2\text{O}_3$  (Fig. 1) and the crucible could be raised by a pneumatic system. During the growth experiment the crucible was placed in the middle of the hot zone of the furnace. At the end of the growth experiment the crucible was raised by the pneumatic system to a position just outside the furnace tube. The flux was poured out of the crucible, which was allowed to cool outside the furnace. During the pouring of the flux minor quantities solidified on the inside wall of the crucible. Crystals in a surface layer of the melt stuck to the wall of the crucible and were thus not poured out with the melt. To remove the flux, the crucible was placed upside down on a porous disc of magnesium oxide in a platinum bowl, and kept for 3–5 h in a muffle furnace at the same temperature as that at which the growth experiment had been terminated in the vertical growth tube furnace. The crystals were cooled in the muffle furnace to room temperature at a rate of 200 °C h<sup>-1</sup>. After this treatment it was relatively easy to separate the crystals from each other. The crystals grew in a

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Table 1. Crystal growth conditions for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .

Experiment No.	Quantities/g			Mole fraction (%)			Soak temp. and time /( $^{\circ}\text{C}/\text{h}$ )	Cooling rate/ $^{\circ}\text{C h}^{-1}$	Flux pouring at temp./ $^{\circ}\text{C}$	Flux separation temp. and time /( $^{\circ}\text{C}/\text{h}$ )	Size of largest crystal /mm
	$\text{YBa}_2\text{Cu}_3\text{O}_7$	$\text{BaCO}_3$	$\text{CuO}$	$\text{YO}_{1.5}$	$\text{BaO}$	$\text{CuO}$					
1	5.27	55.3	52.3	0.8	28.2	71.0	1010/1	1	935	937/21	3×3×0.2
2	12.0	110.6	104.6	0.9	30.0	69.1	1010/15	1	930	930/5	4×2×0.5
4	20.0	111.0	105.0	1.46	30.10	68.45	1010/5	1	930	930/6	1×1×0.2
6	14.0	78.9	127.3	0.99	20.78	78.72	1050/12	1	930	950/10	4×4×0.2
7	14.0	111.0	105.0	1.04	30.00	68.94	1050/12	1	930	950/2	4×3×0.2
8	14.0	131.0	105.0	1.00	33.46	65.54	1050/12	1	930	930/8	$\text{BaCuO}_2$
9	14.0	111.0	114.5	0.99	28.38	70.63	1010/15	5	930	930/8	5×5×0.1
	$\text{Y}_2\text{O}_3$	$\text{BaCO}_3$	$\text{CuO}$								
10	11.28	64.0	45.8	10.00	32.43	57.58	1000/5	1	920	<sup>a</sup>	
11	11.30	122.4	101.8	5.00	31.00	64.00	1020/5	1	920	930/10	2×2×0.8
12	6.80	122.4	105.0	3.00	31.00	66.00	1020/5	1	920	930/10	2×1×0.3
13	11.30	114.5	105.0	5.00	29.00	66.00	1020/5	1	920	930/10	<sup>b</sup>
14	6.78	110.5	109.8	3.00	28.00	69.00	1020/5	1	920	930/10	<sup>b</sup>
15	4.52	110.49	111.39	2.00	28.00	70.00	1010/5	1	930	930/3	<sup>b</sup>
21	2.03	114.75	111.40	0.90	29.10	70.00	1010/5	1	930	930/5	1×1×0.5
27	3.39	171.69	167.03	1.00	29.00	70.00	1010/5	0.5	930	930/3	4×3×0.5
32	3.39	165.77	169.42	1.00	28.00	71.00	1010/5	0.5	920	920/3	10×6×1.5
33	3.39	165.77	169.42	1.00	28.00	71.00	1010/5	0.5	920	920/3	7×5×0.8

<sup>a</sup>Insufficient flux. <sup>b</sup>Flux partially melted. Crystals less than 1 mm of largest dimension.

Table 2. Crystal growth conditions for  $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .

Experiment No.	Quantities/g			Mole fraction (%)			Soak temp. and time /( $^{\circ}\text{C}/\text{h}$ )	Cooling rate/ $^{\circ}\text{C h}^{-1}$	Flux pouring at temp./ $^{\circ}\text{C}$	Flux separation temp. and time /( $^{\circ}\text{C}/\text{h}$ )	Size of largest crystal /mm
	$\text{Pr}_6\text{O}_{11}$	$\text{BaCO}_3$	$\text{CuO}$	$\text{PrO}_{1.5}$	$\text{BaO}$	$\text{CuO}$					
17	6.81	110.51	111.40	2.00	28.00	70.00	1010/5	1	930	930/3	4×4×0.2
23	3.06	114.75	111.40	0.90	29.10	70.00	1010/5	1	930	930/5	6×6×0.2
29	5.11	171.69	167.03	1.00	29.00	70.00	1010/5	0.5	930	930/5	5×5×1.0
	$\text{Nd}_2\text{O}_3$	$\text{BaCO}_3$	$\text{CuO}$	$\text{NdO}_{1.5}$	$\text{BaO}$	$\text{CuO}$					
18	6.73	110.51	111.41	2.00	28.00	70.00	1010/5	1	930	930/3	4×4×0.5
24	3.03	114.75	111.40	0.90	29.10	70.00	1010/5	1	930	930/5	8×5×0.5
28	5.05	171.69	167.03	1.00	29.00	70.00	1010/5	0.5	930	930/3	5×4×0.6
	$\text{Gd}_2\text{O}_3$	$\text{BaCO}_3$	$\text{CuO}$	$\text{GdO}_{1.5}$	$\text{BaO}$	$\text{CuO}$					
19	7.25	110.49	111.42	2.00	28.00	70.00	1010/5	1	930	930/3	1×1×0.5
25	3.25	114.75	111.40	0.90	29.10	70.00	1010/5	1	930	930/3	2×2×0.2
34	5.44	165.77	169.42	1.00	28.00	71.00	1010/5	0.5	920	920/5	10×5×0.7
	$\text{HoBa}_2\text{Cu}_3\text{O}_7$	$\text{BaCO}_3$	$\text{CuO}$	$\text{HoO}_{1.5}$	$\text{BaO}$	$\text{CuO}$					
3	14.0	110.6	104.6	0.95	30.00	69.05	1010/5	1	930	930/5	3×2×0.5
5	19.0	110.0	105.0	1.32	30.07	68.61	1010/5	1	930	930/5	3×2×1.5
	$\text{Ho}_2\text{O}_3$	$\text{BaCO}_3$	$\text{CuO}$	$\text{HoO}_{1.5}$	$\text{BaO}$	$\text{CuO}$					
16	4.16	110.50	108.20	1.13	28.83	70.04	1010/5	1	930	930/3	3×1×0.5
36	5.67	165.42	169.42	1.00	28.00	71.00	1010/5	0.5	920	920/5	8×6×1.5
	$\text{Yb}_2\text{O}_3$	$\text{BaCO}_3$	$\text{CuO}$	$\text{YbO}_{1.5}$	$\text{BaO}$	$\text{CuO}$					
26	3.55	114.75	111.40	0.90	29.10	70.00	1010/5	1	930	930/3	<sup>a</sup>
35	5.91	165.77	169.42	1.00	28.00	71.00	1010/5	0.5	920	920/5	<sup>a</sup>

<sup>a</sup>No large crystals.

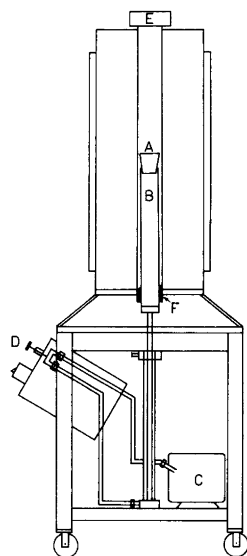


Fig. 1. Sketch of the tube furnace used in the crystal growth experiments. The pneumatic system can lift the crucible 60% of the length of the furnace tube. (A) Crucible, (B)  $\text{Al}_2\text{O}_3$  tube to support the crucible, (C) compressor from refrigerator, (D) valve to release the pneumatic pressure so that the tube is lowered to the middle of the furnace, (E) ceramic block to prevent draught in the furnace tube, (F) space between furnace tube and support rod, loosely filled by wool of heat-resistant fibres (Kao-wool).

surface layer of the melt and at the bottom of the crucible, and it was most difficult to separate the latter crystals from each other.

From each growth experiment a few crystals were selected, crushed and used for recording the X-ray powder pattern on a Stoe diffractometer with a position-sensitive detector, and using  $\text{Cu } K\alpha_1$  radiation ( $\lambda = 1.540598 \text{ \AA}$ ), as reported previously.<sup>21</sup> All samples of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and  $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$  had powder patterns indicating tetragonal symmetry. The unit cell parameters were determined in a profile refinement by the Rietveld method,<sup>24</sup> using the least-squares program EDINP<sup>25</sup> with scattering lengths from Ref. 26, and the results are listed in Table 3. Starting parameters for these calculations were taken from the tetragonal structure of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .<sup>27</sup> A selection of single crystals of  $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$  were annealed in oxygen in the temperature range 540–420 °C for 7 days. The unit cell parameters of the annealed crystals were determined as

above, using the orthorhombic structure of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ,<sup>28</sup> as starting parameters for the calculations. The transition temperature to a superconducting state was measured on a Faraday balance, and the results are also listed in Table 3.

## Results and discussion

Shamoto<sup>3</sup> used a BaO content of 32.5% and  $\text{YO}_{1.5}$  contents from 5 to 15%, and claimed to have obtained crystals (of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ) of sizes from  $5 \times 5 \times 2$  to  $6 \times 6 \times 3 \text{ mm}^3$ . Attempts to reproduce these growth conditions were not successful. At  $\text{YO}_{1.5}$  contents above 2% it was difficult to have the whole charge melted at 1010 °C, and the growth experiments Nos. 10–15 (Table 1) were rather unsuccessful. With  $\text{YO}_{1.5}$  contents less than 2% and a flux composition close to the composition of the eutectic, 72% CuO, of the binary system CuO–BaO, the crystal growth experiments gave the largest crystals of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , No. 32 in Table 1. At first, polycrystalline  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (and  $\text{REBa}_2\text{Cu}_3\text{O}_7$ ) was used in the charges, but this is not necessary in growth experiments where all the charge is melted, and growth experiments where yttrium (or RE) was added to the charge as  $\text{Y}_2\text{O}_3$  (or  $\text{RE}_2\text{O}_3$ ) worked just as well. In all the charges  $\text{BaCO}_3$  was used. The prereaction of the mixtures at 850 °C resulted in a volume reduction, but the mixtures still contained considerable quantities of  $\text{BaCO}_3$  according to X-ray powder patterns of the mixtures. The volume reduction facilitated the production of pellets of the mixtures, and by piling the pellets in the  $\text{Al}_2\text{O}_3$  crucibles it was possible to avoid wetting of the upper parts of the inside wall of the crucibles with the flux, and creeping of the flux out of the crucibles. In the growth experiments the crucibles were up to half-filled with flux. Decantation of the flux, combined with absorption of the rest of the flux by a porous magnesium oxide ceramic, made separation of the grown single crystals from each other easy.

Growth experiments with  $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (Table 2) resulted in large crystals of  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ,  $5 \times 5 \times 1.0 \text{ mm}^3$ ,  $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ,  $8 \times 5 \times 0.5 \text{ mm}^3$ ,  $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ,  $10 \times 5 \times 0.7 \text{ mm}^3$ , and  $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ,  $8 \times 6 \times 1.5 \text{ mm}^3$ . Formation of large crystals of  $\text{YbBa}_2\text{Cu}_3\text{O}_{7-\delta}$  was not observed.

A detailed characterization of single crystals of  $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (RE = Y and Ho) using single-crystal neutron diffraction and electron microprobe analysis<sup>29</sup> showed that the crystals contained Al in the Cu1 site, and

Table 3. Unit cell parameters (in  $\text{\AA}$ ) of tetragonal and orthorhombic  $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and transition temperature to superconductivity.

Compound	Crystals as grown, space group $P4/mmm$ (No. 123)		Crystals annealed in oxygen, space group $Pmmm$ (No. 47)			$T_c/\text{K}$
	a	c	a	b	c	
$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$	3.865(1)	11.704(2)				
$\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$	3.921(1)	11.757(4)				
$\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$	3.914(1)	11.736(4)				
$\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$	3.885(1)	11.729(2)				
$\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$	3.870(1)	11.780(2)	3.844(2)	3.912(2)	11.689(7)	85

that the compositions were  $\text{YBa}_2\text{Cu}_{2.874(8)}\text{Al}_{0.10(1)}\text{O}_{6.31(2)}$  and  $\text{HoBa}_2\text{Cu}_{2.890(8)}\text{Al}_{0.11(1)}\text{O}_{6.53(2)}$ , respectively. The aluminium in the crystals originates from the  $\text{Al}_2\text{O}_3$  crucibles.

**Acknowledgements.** This work was supported with a grant from the Danish Natural Science Research Council concerning investigation of high- $T_c$  superconducting compounds. *Teknologistyrelsen* is thanked for making the Stoe diffractometer available to us. Miss C. Kristensen, Mrs. P. B. Jensen, Mrs. M. A. Chevallier, Mrs. C. Secher, Mr. P. Christensen, Mr. S. Wann and Mr. N. J. Hansen are thanked for valuable assistance.

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Received February 14, 1992.