

# Preparation and Characterization of High- $T_c$ Oxides. $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{REBa}_2\text{Cu}_3\text{O}_7$

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The high- $T_c$  oxides  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{REBa}_2\text{Cu}_3\text{O}_7$  (RE = Nd, Gd, Ho and Yb) were prepared by solid state reactions at 950 °C between  $\text{Y}_2\text{O}_3$  ( $\text{RE}_2\text{O}_3$ ),  $\text{BaCO}_3$  and  $\text{CuO}$ . They all have the orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_7$  structure, and the unit cell parameters were determined from the X-ray powder patterns by a least-squares profile fit procedure. The rate of reaction of a  $\text{Y}_2\text{O}_3$ - $\text{BaCO}_3$ - $\text{CuO}$  mixture at 950 °C was investigated by X-ray diffraction, and  $\text{Y}_2\text{BaCuO}_5$  was found to be formed as an intermediate phase before the end product  $\text{YBa}_2\text{Cu}_3\text{O}_7$  was obtained as a pure phase. The  $T_c$  for superconductivity was measured by a four-point probe method. All the compounds investigated have  $T_c$  in the range 70-90 K and show the Meissner effect. Additional measurements of  $T_c$  were made with a SQUID unit.

The investigation by Bednorz and Müller<sup>1</sup> of compounds formed from the  $\text{BaO}$ - $\text{La}_2\text{O}_3$ - $\text{CuO}$  system which have the  $\text{K}_2\text{NiF}_4$  structure and which showed superconductivity with onset temperatures in around 30 K created considerable interest in research in related oxide systems. Early this year, Wu *et al.*<sup>2</sup> discovered a compound,  $\text{YBa}_2\text{Cu}_3\text{O}_{9-\delta}$ , formed in the  $\text{BaO}$ - $\text{Y}_2\text{O}_3$ - $\text{CuO}$  system that showed superconductivity with onset temperature around 90 K. The phase relations of this ternary system at about 950 °C were investigated by Steinfink *et al.*,<sup>3</sup> and crystal structure investigations of the superconducting phase indicated the formula  $\text{YBa}_2\text{Cu}_3\text{O}_{7\pm x}$ .<sup>4-7</sup> The transition temperature for superconductivity is related to the non-stoichiometry, and thus to the heat treatment of the samples during preparation.<sup>7,8</sup> The fact that this compound is a superconductor at temperatures well above the boiling point of liquid nitrogen has resulted in massive efforts in technological application of the compound and in research aimed at

discovering new compounds with even higher transition temperatures for superconductivity. Substitution of yttrium with rare earth atoms results in the compounds  $\text{REBa}_2\text{Cu}_3\text{O}_7$ , which also have transition temperatures in the vicinity of 90 K.<sup>9-11</sup> It has also been reported that substitution of O with F results in an increase in  $T_c$  to approximately 155 K.<sup>12</sup> A fundamental understanding of why these compounds are superconductors as well as a theory for superconductors are not at hand. It is, however, assumed that the superconductivity of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is due to the mixed valence state of Cu. This valence state may be modified by substitution of atoms in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  with other atoms.

The present work reports the preparation and characterization of some materials with the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  structure. Conventional solid-state preparative procedures were applied instead of co-precipitation of the starting materials from aqueous solutions.<sup>13</sup>

Table 1. Transition temperature for superconductivity (K) and unit cell parameters (Å) of compound with the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  structure.

Compound	$T_c$	$a$	$b$	$c$
$\text{YBa}_2\text{Cu}_3\text{O}_7$	91	3.835(1)	3.884(1)	11.681(2)
$\text{Y}_{0.95}\text{Ce}_{0.05}\text{Ba}_2\text{Cu}_3\text{O}_7$		3.829(1)	3.886(1)	11.657(4)
$\text{Y}_{0.70}\text{Pr}_{0.30}\text{Ba}_2\text{Cu}_3\text{O}_7$		3.827(1)	3.893(1)	11.680(3)
$\text{PrBa}_2\text{Cu}_3\text{O}_7$		3.878(1)	3.940(1)	11.761(2)
$\text{NdBa}_2\text{Cu}_3\text{O}_7$	69	3.885(1)	3.929(1)	11.777(3)
$\text{GdBa}_2\text{Cu}_3\text{O}_7$	92	3.856(1)	3.896(1)	11.690(3)
$\text{HoBa}_2\text{Cu}_3\text{O}_7$	87	3.831(1)	3.889(1)	11.664(5)
$\text{YbBa}_2\text{Cu}_3\text{O}_7$	86	3.803(2)	3.880(3)	11.628(9)

## Experimental and results

**Chemistry.** The following chemicals were used in the syntheses:  $\text{BaCO}_3$  (Merck, *p.a.*),  $\text{CuO}$  (Baker, Analyzed),  $\text{Y}_2\text{O}_3$  (Fluka, *puriss.*),  $\text{Pr}_6\text{O}_{11}$  (Thorium Limited),  $\text{Nd}_2\text{O}_3$  (Koch-Light),  $\text{Gd}_2\text{O}_3$  (Fluka, *puriss.*),  $\text{Ho}_2\text{O}_3$  (Fluka, *puriss.*),  $\text{Yb}_2\text{O}_3$  (Fluka, *puriss.*). In addition,  $\text{Ce}$  (Fluka, 99.9%) was used to prepare  $\text{CeO}_2$ .

The nominal compositions of the compounds prepared are listed in Table 1. In each preparation 0.010 mol of the compound was made, and with  $\text{YBa}_2\text{Cu}_3\text{O}_7$  as an example the procedure was the following:  $\text{Y}_2\text{O}_3$  was preheated in an alumina or platinum crucible to 900 °C for at least 30 min to decompose any carbonate or hydroxide. The following quantities of reactants were weighed out: 0.0050 mol  $\text{Y}_2\text{O}_3$  (1.129 g), 0.020 mol  $\text{BaCO}_3$  (3.947 g) and 0.030 mol  $\text{CuO}$  (2.387 g). These reactants were ground together in a porcelain or agate mortar and fired twice. For the first firing the mixture was (1) packed firmly into an  $\text{Al}_2\text{O}_3$  or Pt crucible, or (2) pressed into a pellet of 1–2 cm diameter and then placed in a crucible. The mixture was then heated in air in a crucible furnace at 950 °C for 12 h, cooled to 600 °C over 3 h, and then cooled to room temperature outside the furnace. The product obtained after the first firing was a gray-black sintered lump that was ground in a porcelain mortar and pressed into pellets approximately 1 cm in diameter and 2–3 mm in thickness applying a force of 6 tons. The pellets were then annealed in a tube furnace in a stream of oxygen for 12 h at 950 °C, cooled to 600 °C over 3–4 h, and then cooled to a temperature between 350 °C and 250 °C over 3–4 h. The pellets were removed from the tube fur-

nace and quenched in air to room temperature. The product was a hard gray-black ceramic material with a slightly metallic luster resembling that of silicon. The samples so prepared are slowly affected by water and  $\text{CO}_2$  in the atmosphere and should be stored in closed containers, preferably over  $\text{BaO}$  or similar reagents.

**X-Ray diffraction.** X-Ray diffraction patterns were recorded on a Stoe diffractometer with a position-sensitive detector using  $\text{CuK}\alpha_1$  ( $\lambda = 1.540598 \text{ \AA}$ ) or  $\text{CoK}\alpha_1$  ( $\lambda = 1.78897 \text{ \AA}$ ) radiation. The diffractometer was calibrated using a silicon standard with the unit cell parameter  $a_{\text{Si}} = 5.43050 \text{ \AA}$ .

The compounds investigated have the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  structure, and the unit cell parameters listed in Table 1 were derived from a profile fit to the powder patterns with the calculated powder patterns based on a model of the structure, and using a least-squares procedure proposed by Rietveld.<sup>14</sup> In these calculations the atomic scattering factors reported by Cromer and Mann<sup>15</sup> and the program EDINP were used.<sup>16</sup>

The unit cell parameters of the  $\text{REBa}_2\text{Cu}_3\text{O}_7$  compounds show, as expected, a variation due to the lanthanide contraction. All compounds listed in Table 1 were prepared as pure phases with the exception of  $\text{YbBa}_2\text{Cu}_3\text{O}_7$ , which contained a considerable quantities of  $\text{CuO}$  and the green compound  $\text{Yb}_2\text{BaCuO}_5$ .<sup>17</sup> This latter compound was identified by a calculation of the powder pattern with the program LAZY-PULVERIX,<sup>18</sup> using the unit cell parameters  $a = 12.059$ ,  $b = 5.612$ ,  $c = 7.054 \text{ \AA}$ , the space group  $Pnma$ , and the model of the structure reported by Michel and Raveau.<sup>17</sup> In a second preparation carried

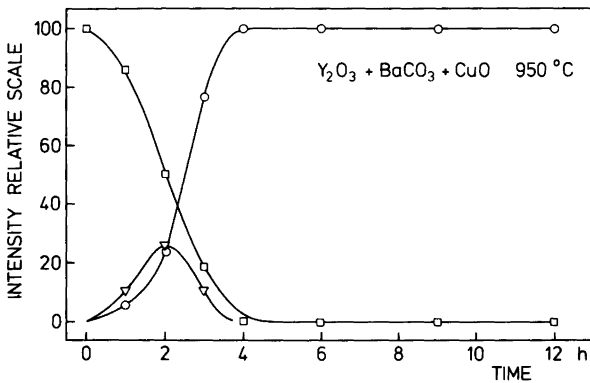


Fig. 1. Rate of reaction of a Y<sub>2</sub>O<sub>3</sub>-BaCO<sub>3</sub>-CuO mixture at 950°C to produce YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>. The symbols indicate BaCO<sub>3</sub> (□), Y<sub>2</sub>BaCuO<sub>5</sub> (▽) and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> (○).

out by annealing at 1000°C for 100 h, a sample was obtained in which YbBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> was the main product and Yb<sub>2</sub>BaCuO<sub>5</sub> was a minor impurity.

*Rate of reaction of a Y<sub>2</sub>O<sub>3</sub>-BaCO<sub>3</sub>-CuO mixture at 950°C.* The rate of reaction of a Y<sub>2</sub>O<sub>3</sub>-BaCO<sub>3</sub>-CuO mixture corresponding to 0.010 mol of the end product YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> was studied at 950°C. The mixture was pressed into pellets and placed in a platinum crucible in a crucible furnace. The reaction time was from 1 to 12 h. X-Ray powder diffraction patterns of the samples were recorded as described above, and from these patterns the quantities of the different solids in the samples were determined. The results of this investigation are displayed in Fig. 1. Of the three solids in the mixture, Y<sub>2</sub>O<sub>3</sub> is consumed fastest, and after 1 h Y<sub>2</sub>O<sub>3</sub> was not detectable in the powder diffraction pattern. The

green compound Y<sub>2</sub>BaCuO<sub>5</sub> is formed as an intermediate phase. It is present in greatest quantity after 2 h and is completely consumed after 4 h at 950°C.

BaCO<sub>3</sub> is completely consumed after 4 h, and the only crystalline phase present is then YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>. The solid state reaction is thus rather fast at 950°C for the mixture when pressed into pellets. When the mixture is only loosely packed in the crucible, a considerably longer time at 950°C is necessary to obtain transformation to YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>.

When the temperature of the mixture is increased to approximately 1050°C the compound YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> melts, and on cooling the compounds CuO and Y<sub>2</sub>BaCuO<sub>5</sub> are present. The X-ray powder pattern of a sample heated as described above indicated the presence of only these two compounds.

Fig. 2. Rate of reaction of a Yb<sub>2</sub>O<sub>3</sub>-BaCO<sub>3</sub>-CuO mixture at 950°C. The symbols indicate Yb<sub>2</sub>O<sub>3</sub> (◇), BaCO<sub>3</sub> (□) and Yb<sub>2</sub>BaCuO<sub>5</sub> (▽).

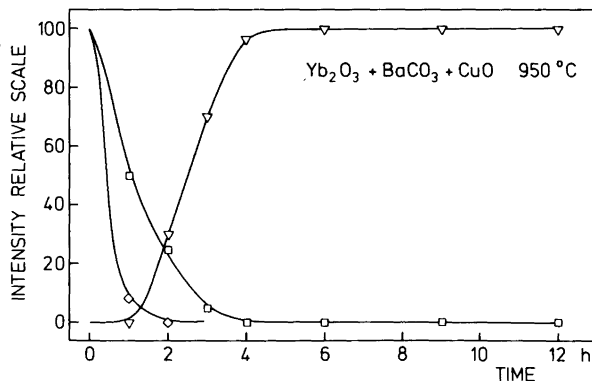
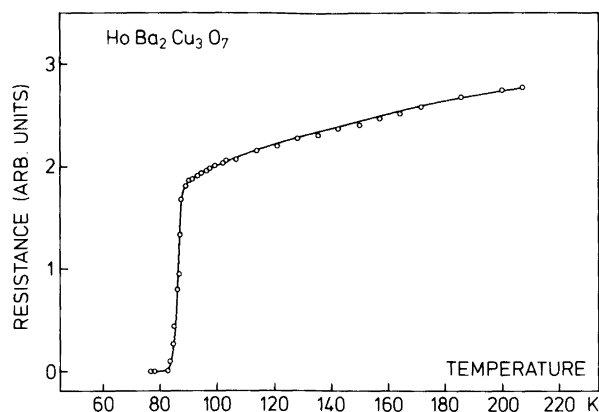


Fig. 3. Electrical resistance of  $\text{HoBa}_2\text{Cu}_3\text{O}_7$  vs. temperature. The transition temperature 87 K is the mid-point value of the transition with a typical total width of 5 K.



*Rate of reaction of a  $\text{Yb}_2\text{O}_3$ - $\text{BaCO}_3$ - $\text{CuO}$  mixture of  $950^\circ\text{C}$ .* The rate of reaction of a  $\text{Yb}_2\text{O}_3$ - $\text{BaCO}_3$ - $\text{CuO}$  mixture at  $950^\circ\text{C}$  was studied in the same way as described above for the yttrium-containing system, and the results of the investigation are displayed in Fig. 2.  $\text{Yb}_2\text{O}_3$  is consumed faster than  $\text{BaCO}_3$ , and after 2 and 4 h, respectively, no traces of these two compounds were found. The reaction product formed is  $\text{Yb}_2\text{BaCuO}_5$ , and the formation of  $\text{YbBa}_2\text{Cu}_3\text{O}_7$  is hardly detectable during the first 12 h of the solid state reaction. The compound  $\text{BaYb}_2\text{O}_4$  is possibly formed as an intermediate phase before the formation of  $\text{Yb}_2\text{BaCuO}_5$  takes place.

*Physical measurements.* The transition temperature for superconductivity,  $T_c$ , was measured by a four-point probe method with the sample mounted on a brass cold finger cooled with liquid nitrogen. The current leads were soldered to the specimens with indium. Fig. 3 displays, as an example, the resistance vs. temperature curve for one of the samples examined. Measurements of  $T_c$  were also made with a SQUID unit. The values found by the four-point probe method and the DC-magnetization (SQUID) method are listed in Table 1. The compound  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  showed no transition at temperatures down to 2 K.

## Discussion

The solid-state preparative procedure employed in this work leads to rather fast formation of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  at  $950^\circ\text{C}$  from a mixture of  $\text{Y}_2\text{O}_3$ ,

$\text{BaCO}_3$  and  $\text{CuO}$ , and the compound  $\text{Y}_2\text{BaCuO}_5$  is formed as an intermediate phase. The corresponding preparation of  $\text{YbBa}_2\text{Cu}_3\text{O}_7$  is much slower, and an intermediate phase,  $\text{Yb}_2\text{BaCuO}_5$ , is also formed in this case. At least 100 h annealing at  $1000^\circ\text{C}$  is necessary to obtain a sample with a considerable content of  $\text{YbBa}_2\text{Cu}_3\text{O}_7$ . The difference in base character of  $\text{Y}_2\text{O}_3$  and  $\text{Yb}_2\text{O}_3$  may possibly explain these findings.

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