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Influence of Complexing Agents on Properties of $YBa_2Cu_4O_8$ Superconductors Prepared by the Sol-Gel Method

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A systematic study of sol-gel technique synthesized $YBa_2Cu_4O_8$ (124) is presented using six different complexing agents: ascorbic acid, citric acid, 1,2-ethanediol, poly(vinyl alcohol), succinic acid, and tartaric acid. These complexing agents were found to influence significantly the characteristics of both the precursors and the product superconducting material, in particular the homogeneity. The 124 phase was formed by a solid state reaction at 780°C in flowing oxygen after decomposition of the organic anions at lower temperature. The dried precursor gels and final products were characterized by thermogravimetry, X-ray powder diffraction, scanning and transmission electron microscopy, and magnetic susceptibility measurements. Syntheses using either 1,2-ethanediol or tartaric acid yielded monophasic $YBa_2Cu_4O_8$ powder, with the highest diamagnetic volume fractions and superconducting transition temperatures (onset) at 79–80 K.

INTRODUCTION

The importance of chemical routes in the preparation of superconducting materials is well documented for both bulk and thin-film samples (1–3). Among the numerous studies on high-T_c superconducting compounds, those concerning the Y–Ba–Cu–O system are the most frequent so far. Catania *et al.* (4) compared different sol-gel syntheses of the superconducting $YBa_2Cu_3O_{7-x}$ (123) phase using molecular precursors in organic medium and ionic precursors in aqueous medium. They concluded that the superconducting properties of the materials depend significantly on the preparation method. Using oxalate coprecipitation for the preparation of different types of Y–Ba–Cu–O powders, they reported the concentration of the starting materials and the starting solvent as well as different heat treatments to be important (5–7).

Bonoldi *et al.* studied the role of the initial reagents in the synthesis of $YBa_2Cu_4O_8$ (124) using eight different combinations of salts and oxides of the three elements to make up the initial composition (8). They found that the initial reaction stage is crucial for the preparation of superconducting materials. In contrast, Sosa *et al.* observed no significant variation in superconducting characteristics of $YBa_2Cu_3O_7$ samples prepared under different oxygen flows and cooling rates (9).

Previous studies of a relatively simple aqueous sol-gel process, with acetate/tartrate precursor gels to synthesize pure as well as europium- and iron-substituted samples, have shown that the sol-gel method works well for the 124 phase (10–12). The use of tartaric acid as complexing agent prevents the segregation of metal acetates during synthesis, and transparent solutions and homogeneous gels can thus be easily obtained. However, no systematic study concerning the influence of complexing agents on the properties of superconducting materials prepared by the sol-gel technique has been reported. Therefore, we found it interesting to investigate the influence of different complexing agents on the characteristics of the 124 material prepared by the sol-gel method. In order to prevent partial crystallization of the metal salts we chose complexing agents which contained a various number of hydroxo and/or carboxyl groups, namely, ascorbic acid, citric acid, 1,2-ethanediol (glycol), poly(vinyl alcohol), and succinic acid. To facilitate the interpretation, we included a comparison of the results with those of a previous study with tartaric acid as complexing agent (10).

EXPERIMENTAL

We used the reported synthesis route for the preparation of precursor gels and superconducting 124 samples by the sol-gel technique, starting from metal acetates and Y_2O_3 (10). Six different high-purity organic substances were used as complexing agents: (1) ascorbic acid, (2) citric acid, (3) 1,2-ethanediol, (4) poly(vinyl alcohol), (5) succinic acid, and (6) tartaric acid. A molar ratio of 0.44 (complexing agent: Cu) was selected in all cases (10). The complexing

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TABLE 1
TG Data on the Ternary Y–Ba–Cu–O Gels Obtained from Different Precursors

Synthesis	Temperature range and weight loss Evolution of water	 Main decomposition	 Total weight loss at 880°C
1, ascorbic acid	Below 175°C, 6.1%	(175–250°C), 12.9%; (250–360°C), 19.6%	42.6%
2, citric acid	Below 175°C, 6.6%	(175–230°C), 23.1%; (230–345°C), 16.0%	49.7%
3, 1,2-ethanediol	Below 175°C, 6.6%	(175–230°C), 18.4%; (230–380°C), 17.9%	48.6%
4, poly(vinyl alcohol)	Below 175°C, 4.7%	(175–350°C), 34.0%; (350–380°C), 22.4%	64.5%
5, succinic acid	Below 175°C, 6.0%	(175–265°C), 27.8%; (265–380°C), 14.0%	51.6%
6, tartaric acid	Below 175°C, 6.3%	(175–240°C), 21.9%; (240–380°C), 15.8%	47.8%

agents ascorbic acid and poly(vinyl alcohol) gave turbid gels. In the case of succinic acid a small amount of precipitate was formed during the solvent evaporation. The other three reagents, 2, 3, and 6, yielded viscous and transparent gels. The six different gels were then decomposed at low temperature according to (10). The powders were then heated in flowing oxygen at 780°C for 10 h, reground intermediately and further heated for 30 h.

Thermogravimetric (TG) measurements of the gel decomposition were carried out with a Perkin–Elmer TGA-7 analyzer, using flowing oxygen and a heating rate of 5°C min^{-1}. The thermal stability of the final product in oxygen and argon atmospheres was confirmed by TG measurements, using heating and cooling rates of 5°C min^{-1}. The sample weight was 25–45 mg and the temperature range 40–1000°C in all TG experiments.

The phase purity and the crystallinity of the products were studied by X-ray powder analysis with a Philips MPD 1880 diffractometer. Cell parameters were refined from X-ray powder data obtained with a Guinier-Hägg focusing camera with $CuK\alpha_1$ radiation ($\lambda = 1.54059$ Å). Finely powdered silicon, $a = 5.430880$ Å (13), was used as internal standard. The reflection intensities were evaluated with an automatic film scanner (14), and the SCANPI program (15) was used for processing the data. Lattice constants were calculated with the PIRUM program (16).

The cation content was analyzed by energy-dispersive spectrometry (EDS) in a JEOL 820 scanning electron microscope (SEM), using the *L*-lines for Y and Ba and the *K*-lines for Cu. To confirm these results and to obtain electron diffraction patterns, some synthesis products were also studied by transmission electron microscopy (TEM) in a JEOL 2000FX microscope equipped with an EDS-detector (LINK QX200) in the high angle (70°) position.

The diamagnetic susceptibility was determined with a Lake Shore 7000 AC susceptometer. The frequency was 125 Hz and the field was 250 Am^{-1} (3 Oe) in the temperature range 15–110 K.

RESULTS AND DISCUSSION

Thermal Decomposition of Dried Gels

TG measurements showed that in all cases the thermal decomposition proceeded in a similar way. Decomposition started below 175°C with a loss of crystallization water and/or water from the coordination sphere of the metal complexes. Weight losses took place in several steps between 175°C and 380°C, due to a decomposition of the gels according to $CuR \rightarrow CuO$ or $CuR \rightarrow Cu_2O$, $YR \rightarrow Y_2O_3$ and $BaR \rightarrow BaCO_3$ (10, 17). Finally, a weight loss could be attributed to the decomposition of $BaCO_3$ to BaO starting at approximately 780°C. Data on the thermal decomposition of gels, synthesized using different complexing agents, are summarized in Table 1.

X-Ray Diffraction

When the typical XRD patterns of the different synthesis products are compared (Figs. 1a–1e), it can be seen that only the use of 1,2-ethanediol (Fig. 1c) and tartaric acid (10) yields a single 124 phase. A separation of the characteristic reflections (017, 111), at the 2Θ values 32° and 33°, and (0014, 020, 200), in the 2Θ range 46°–47°, is evident in Fig. 1c. These results are in a good agreement with those previously published for the 124 phase synthesized by using tartaric acid in the gel formation process (10).

X-ray diffraction patterns of the specimens produced by using ascorbic, citric, and succinic acids are shown in Figs. 1a, 1b, and 1e, respectively. The diffraction lines are due to the 123 phase (18, 19). The peaks marked with circles indicate a small amount of $BaCuO_2$ and CuO. Probably 124 is formed as well, but it seems that 123 is predominant in these three cases. The 124 phase has been reported to be more stable thermodynamically than 123 at an oxygen pressure of 1 atm (20), but several authors have reported that the less stable 123 is formed before 124, regardless of the Y, Ba, and Cu stoichiometry in the precursor (18, 19, 21, 22). Transformations such as $YBa_2Cu_3O_{7-x} + CuO \rightarrow$

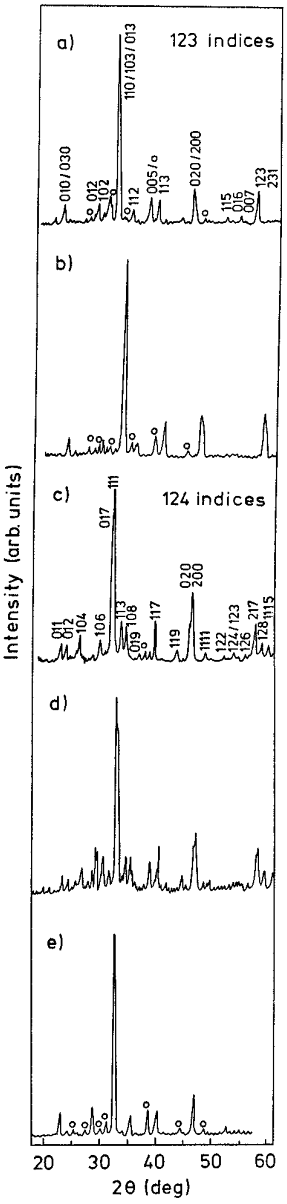

FIG. 1. Powder X-ray diffraction patterns of the prepared Y–Ba–Cu–O samples annealed in flowing oxygen at 780°C for 10 + 30 h from: (a) synthesis 1; (b) synthesis 2; (c) synthesis 3; (d) synthesis 4; (e) synthesis 5.

$YBa_2Cu_4O_{8-x}$ or $4YBa_2Cu_3O_{6.75} \rightarrow 2YBa_2Cu_4O_8 + Y_2BaCuO_5 + 3BaCuO_2$ may therefore be important.

Figure 1d shows an X-ray diffraction pattern of the sample synthesized with poly(vinyl alcohol) as a complexing agent. According to the XRD results and in accordance with literature data (19, 23), it is clear that a mixture of 123 and 124 phases was formed.

The refined parameters of the orthorhombic cell of the two most phase-pure samples are a = 3.846(2) Å, b = 3.870(1) Å, c = 27.236(5) Å for agent 3 and a = 3.844(1) Å, b = 3.8703(7) Å, c = 27.243(5) Å for agent 6.

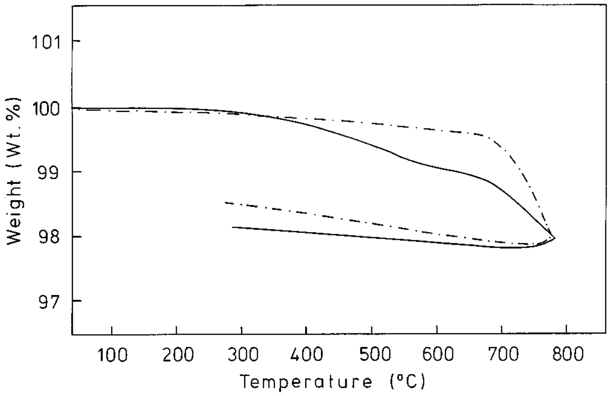

FIG. 2. Thermogravimetric heating and cooling curves in Ar of the Y–Ba–Cu–O samples from syntheses 2 (solid line) and 6 (broken line) (10). Heating and cooling rates were 5°C min^{-1}, and the sample mass was approximately 30 mg.

Thermal Stability

X-ray diffraction analysis revealed variable amounts of 123 and 124 phases in the samples, depending on the preparation method. The structural similarity of 123 and 124 makes it difficult to use XRD to properly distinguish between these two phases, due to overlap of the reflections. It is known, however, that the 123 phase starts to lose oxygen around 330–400°C, depending on the atmosphere, while 124 is stable up to 690°C in argon, up to 830°C in air, and up to 890°C in oxygen (10, 17). Thus, the phase purity of all prepared samples was checked by TG measurements.

Figure 2 shows the TG curves of subsequent heating and cooling cycles in argon atmosphere for two of the synthesized samples, case 2 (solid line) and case 6 (broken line). A decrease in weight at 360°C can be seen in the citric acid case, but no pronounced weight loss occurred below 690°C with tartaric acid. These results indicate that the sample from synthesis 2 contained different phases, while synthesis 6 gave pure 124, in agreement with the XRD results. When cooling the samples in oxygen flow, it seems that the sample prepared with tartaric acid, which contains more 124, takes up oxygen to a larger extent.

The influence of the different complexing agents on the thermal stability in argon of the final superconducting sample is demonstrated in Fig. 3. TG curves of the samples prepared with the complexing agents 1,2-ethanediol and tartaric acid (Fig. 3, curves 3 and 6) show that the weight remained constant up to 690°C except the minor weight losses at low temperature, which may be due to moisture. On the other hand, the samples from syntheses 1, 2, 4, and 5 lost weight between 340°C and 390°C (Fig. 3, curves 1, 2, 4, and 5). This implies that the 123 and 124 phases were both present in the samples, in agreement with the X-ray diffraction analysis. Additionally, an investigation of the

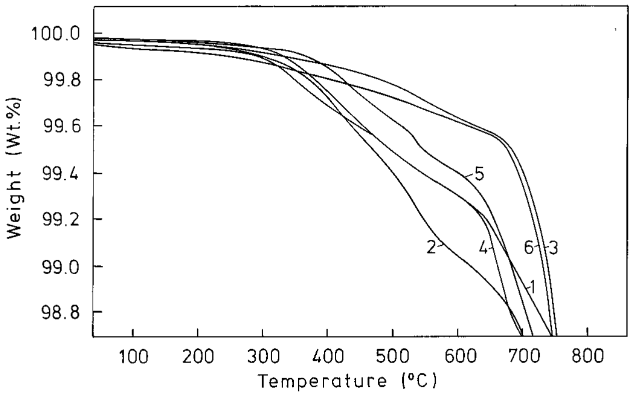

FIG. 3. Thermogravimetric heating curves in Ar of the Y–Ba–Cu–O samples from syntheses 1–6. The heating rate was 5°C min^{-1} and the sample mass was 30–40 mg.

thermal stability of synthesized samples in flowing oxygen led to the same conclusion.

SEM Investigation

During the SEM investigation, EDS analyses were carried out on all of the gel precursors. The results are presented in Table 2; they indicate that the initial stage of preparation is important and that the complexing agent for each system should be selected with care. For example, the precursor composition in cases 1 and 5 was inhomogeneous, as seen from the standard deviations. Numerous particles of the starting materials and different molar ratios of the metals were found. More homogeneous powders were obtained in cases 2 and 4, and the compositions correspond either to 123 or to 124. When 1,2-ethanediol and tartaric acid were used (3 and 6, respectively), however, the syntheses yielded homogeneous precursors with compositions near to the metal ratio in 124.

TABLE 2
EDS Analysis of the Dried Gels, with Standard Deviations within Parentheses

	Molar percentage of metals (%)		
Synthesis	Y	Ba	Cu
1	16(7)	39(9)	45(14)
2	10(3)	24(2)	66(4)
3	14(2)	27(3)	59(5)
4	14(2)	25(6)	61(7)
5	16(7)	34(9)	50(15)
6	14(2)	29.4(4)	57(2)
Starting composition	14.3	28.6	57.1

Note. Number of analyzed particles, $n \approx 10$.

TABLE 3
Formulas of the Final $YBa_2Cu_4O_8$ Samples Calculated from EDS Data Obtained in an SEM

Synthesis	Major phase	Secondary phases
1	$Y_{1.0(1)}Ba_{1.8(2)}Cu_{3.4(4)}O_x$	124, $BaCuO_2$, CuO
2	$Y_{0.9(4)}Ba_{2.1(1)}Cu_{3.5(5)}O_x$	124, CuO
3	$Y_{1.0(4)}Ba_{2.0(1)}Cu_{4.0(4)}O_x$ TEM: $(Y_{1.03(8)}Ba_{2.04(4)}Cu_{3.98(8)}O_x)$	$BaCuO_2$
4	$Y_{0.9(1)}Ba_{2.0(1)}Cu_{3.5(5)}O_x$	124, CuO
5	$Y_{0.8(1)}Ba_{2.2(2)}Cu_{4.3(5)}O_x$	124, $BaCuO_2$, CuO
6	$Y_{0.9(1)}Ba_{2.0(1)}Cu_{4.1(1)}O_x$ TEM: $(Y_{1.14(3)}Ba_{2.07(5)}Cu_{3.83(7)}O_x)$	$BaCuO_2$

Note. The two best samples, 3 and 6, were also analyzed by EDS in a TEM; these results are given within parentheses. Approximately 10 crystallites of each sample were analyzed.

The microstructure and composition of the final products were also studied by means of SEM/EDS. It was seen that all specimens consisted of small grains with diameters <1 μm. Uniform powders with a large surface area were observed, in agreement with other investigations of similar chemical syntheses (4, 7, 21, 24).

EDS analyses of the final superconducting samples showed that the Y–Ba–Cu composition approximated that of the dried gels. Data from the elemental analysis of the obtained crystallites are presented in Table 3. The analysis of these selected crystals was consistent with the results from TG and XRD. It may be concluded that tartaric acid or 1,2-ethanediol are the best complexing agents for sol-gel synthesis of 124. Although the sol-gel technique for synthesizing superconducting oxides is generally based on the ability of hydroxy acids to chelate metal ions, polyfunctional alcohols (e.g., ethylene glycol) as an additional reagent have also been reported to stabilize metal–acid complexes and to form oligomers by esterification (2).

Magnetic Susceptibility

The susceptibility of the samples prepared by syntheses 1–5 was measured. All curves are presented in Fig. 4, showing that a product with the highest diamagnetic volume fraction was formed in case 3 (1,2-ethanediol). It seems that syntheses 1 and 5 gave products with a relatively low superconducting fraction compared to the other routes. Moreover, from a magnified part of Fig. 4 (Fig. 5) it is evident that the superconductors have different onset transition temperatures. Synthesis 3 yielded a product with a superconducting temperature near that reported for 124, which is in agreement with the results from XRD and EDS. The fact that this curve shows a broad transition with two steps is in accordance with the results of Kawachi *et al.* (25), attributing this phenomenon to the small grain size of

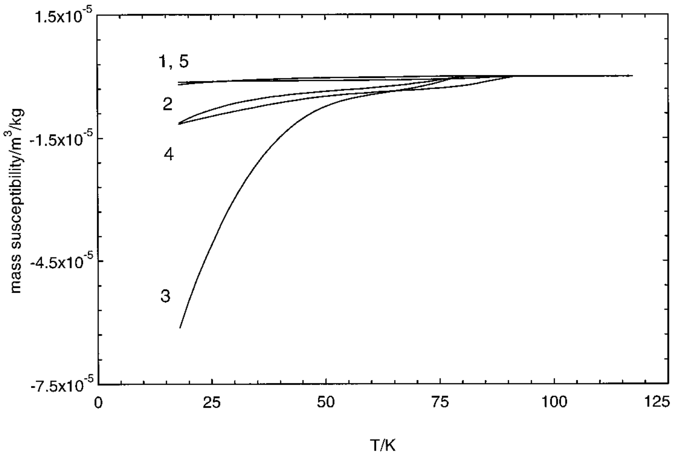

FIG. 4. Magnetic susceptibility in SI units versus temperature for the Y–Ba–Cu–O powders synthesized with complexing agents 1–5.

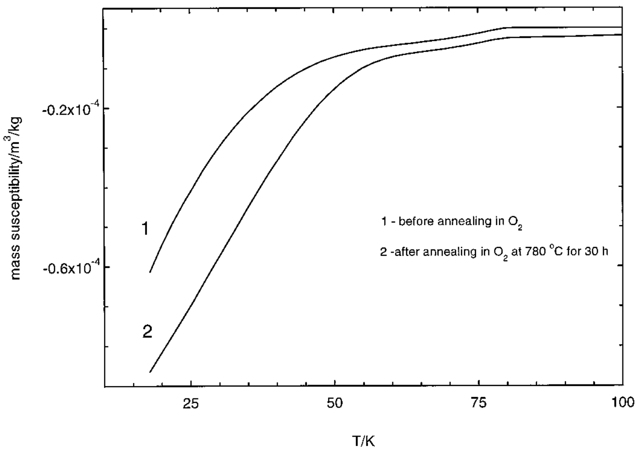

FIG. 6. Magnetic susceptibility measurements of one-year-old 124 powder prepared with 1,2-ethanediol as complexing agent (1), and the same sample reground, pelletized, and reheated in oxygen at 780°C for 30 h (2).

the superconductor, comparable to the penetration depth. Furthermore, a superconducting order is first established inside each grain at T_{C1} ($\cong$80 K), and is then correlated among the grains at T_{C2}. In the present study an effort was made to increase the crystallite size in the two best samples, prepared with the complexing agents 3 and 6. These powders were thus pressed to pellets and reheated in an oxygen flow at 780°C for 30 h. This treatment increased the diamagnetic signal slightly, as seen in Fig. 6.

Transmission Electron Microscopy Study

The two samples, 3 and 6, which were monophasic 124 according to the other investigations were also checked in the analytical TEM. Since no corrections due to sample thickness or density could be made, only thin edges of crystallites were analyzed and minor corrections were applied according to previous analyses of monophasic 123. The average stoichiometry in the crystallites was very near Y : Ba : Cu = 1 : 2 : 4 (see Table 3) and agreed with the results from the SEM analysis. Selected-area electron diffraction photographs were also obtained (Figs. 7a and 7b). The dimensions and symmetries of all the main reflections agreed with the *A*-centered unit cell of 124. It was noticed that in most cases the ED patterns were streaked along c^*, however. The streaking indicates that stacking faults, such as intergrowths of 123 or other homologoues, occur in the structure of 124. Moreover, some diffraction patterns indicated twinning. Figure 7c can be interpreted as a superposition of the 100 and 010 zones. It is therefore possible that not only the small particle size but also disorder due to stacking faults and twinning broadened the superconducting transitions.

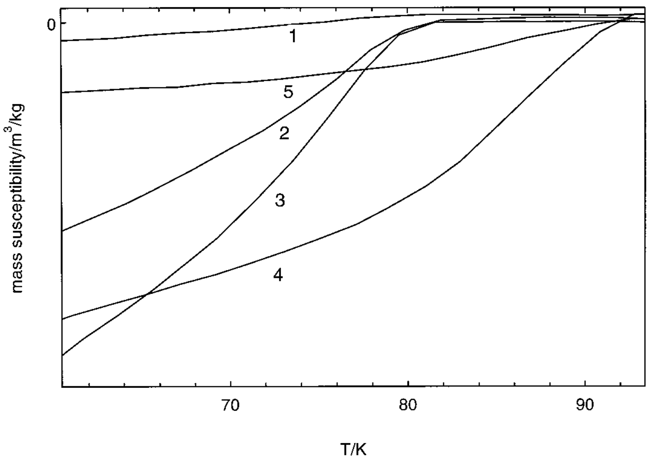

FIG. 5. A magnified part of the susceptibility curves in Fig. 4, showing the superconducting transitions. The samples of 124 were synthesized with the complexing agents 1–5.

CONCLUSIONS

Monophasic 124 powder was synthesized using the complexing agents 1,2-ethanediol or tartaric acid in a sol-gel process followed by a solid state reaction at 1 atm oxygen pressure. The use of tartaric acid as complexing agent has been described earlier, but the successful use of only 1,2-ethanediol has not been previously reported, to our knowledge.

These two samples contained homogeneous 124 crystallites as a major phase, as shown by XRD, SEM with EDS, and TG. T_c(onset) observed by magnetic susceptibility was approximately 80 K, and the superconducting transitions were relatively broad. One-year-old as-synthesized samples had approximately the same properties as fresh

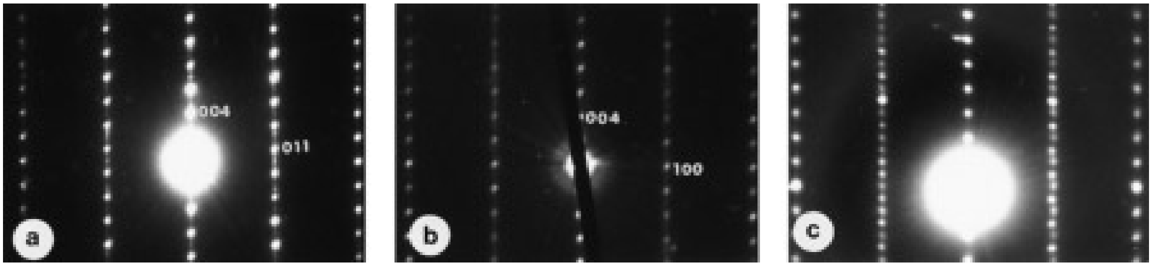

FIG. 7. Selected-area electron diffraction photographs of $YBa_2Cu_4O_8$ synthesized with a sol-gel method using 1,2-ethanediol as complexing agent. The crystallites were aligned along the zone directions [100] (a) and [010] (b), respectively. The pattern (c) shows twinning of the [100] and [010] zones.

ones. Reheating the samples in pellet form improved their superconducting properties slightly. TEM investigations showed that twinning and stacking faults were frequent. It is possible that this disorder and the small grain size are the causes of the broad superconducting transitions.

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