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SYNTHESIS OF $Y_1Ba_2Cu_3O_x$ SUPERCONDUCTING POWDERS BY INTERMEDIATE PHASE REACTIONS

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ABSTRACT

A procedure for synthesizing $Y_1Ba_2Cu_3O_x$ by solid-state reactions has been developed. The method is based on the use of barium compounds, previously synthesized, as intermediate phases for the process. The reaction kinetics of this procedure have been established between 860°C and 920°C. The crystal structure and the presence of second phases have been studied by means of XRD. The sintering behaviour and ceramic parameters were also determined. The orthorhombic type-I structure has been obtained on the synthesized powder and on the sintered bodies after a cooling cycle in air atmosphere. Superconducting transition took place at 91 K. Sintering densities higher than 95% D_{th} were attained at temperatures below 940°C.

1. INTRODUCTION

Since the discovery of High-T_c Superconductivity in the 90 K range in $Y_1Ba_2Cu_3O_x$ compound (1), considerable efforts have been invested toward improving the synthesis process. This represents an important problem, because of the great complexity of the Y_2O_3-BaO-CuO ternary system (2-5). Several routes have been proposed for the consecution of reproducible and reliable synthesis processes, which lead to single-phase superconducting powder and ceramic materials. Most of these routes have two features in common: a) the formation begins from a mixture of three distinct precursors or raw materials; and b) for some of the several steps, barium carbonate is present as a raw material or as an intermediate product from some precursor (6-8). In a previous work (9), a procedure for synthesizing $Y_1Ba_2Cu_3O_x$ via solid-state reaction from intermediate phases was given. In these intermediate phases, the barium cation is fully combined with CuO and/or Y_2O_3 in adequate amounts. By this procedure, $BaCO_3$, which plays a retarding role in the synthesis process, is not present through the reaction pathway. Ruckenstein et al. (10) have studied another of these possible reactions:

$$Y_2Cu_2O_5 + 4BaCuO_2 \longrightarrow 2Y_1Ba_2Cu_3O_x \qquad [1]$$

but the slow formation reaction rate of $Y_2Cu_2O_5$ (4) and the high temperatures in which the reaction [eq. 1] takes place are major problems that hinder their practical application. Better results were obtained for Halasz et al. (11) by means of the use of $Ba_2Cu_3O_5$ as the intermediate synthesized phase, which reacts with Y_2O_3 to give $Y_1Ba_2Cu_3O_x$ according to the reaction sequence:

$$2Ba_2Cu_3O_5 + Y_2O_3 \longrightarrow 2Y_1Ba_2Cu_3O_x. \qquad [2]$$

The reaction [eq. 2] was systematically studied by the present authors in previous work, along with two other possible pathways, based on the use of the oxycarbonates, $Y_2Ba_4O_7.xCO_2$ and $Y_2Ba_2O_5.yCO_2$. The results of the three processes were promising, but the presence of CO_2 in the oxycarbonates was a limiting factor in the reaction kinetics. The third pathway, $Ba_2Cu_3O_5$+ $1/2Y_2O_3$, led to the formation of single-phase $Y_1Ba_2Cu_3O_x$ at 920°C in relatively short times--1 to 2 hours. Nevertheless, the nature of the $Ba_2Cu_3O_5$ synthesis product, which is a mixture of $BaCuO_2$ plus uncombined CuO, gives rise to the formation of intermediate $Y_2Cu_2O_5$ from free Y_2O_3, which was a retarding compound for the reaction.

In the present work, two new reaction pathways have been analyzed for their possible usefulness as adequate synthesis methods for obtaining $Y_1Ba_2Cu_3O_x$, without the presence of barium carbonates or oxycarbonates through the process. Both of them start from stable yttrium-barium phases which react with homogeneous blends of $BaCuO_2$ + CuO, obtained by calcining adequate amounts of $BaCO_3$ and CuO.

2. EXPERIMENTAL METHOD

$BaCO_3$ (Merck), CuO (Merck) and Y_2O_3 (Johnson and Mathey), all of analytical grade, were used as raw materials. Two barium-yttrium compounds were synthesized from stoichiometric mixtures. BaY_2O_4 was obtained from the calcining of the corresponding stoichiometric mixture of $BaCO_3$ and Y_2O_3 at 1350°C for 2 hours, and then quenching to room temperature. $Ba_3Y_4O_9$ was obtained by calcining at 1300°C for 8 hours with subsequent quenching. The calcination temperatures were chosen according to the phase diagram developed by Kwestroo et al. (12). The $BaCO_3$+ 2CuO blend was heat-treated at 920°C for 16 hours, and quenched to room temperature.

The synthesized compound was identified by X-Ray Diffraction (XRD). The powders were ball-milled with isopropanol for 3 hours in a zirconia vibratory mill, and then attrition-milled for 2 hours with alumina balls. Adequate amounts of these compounds were weighted, mixed and homogeneized by wet milling. Isopressed pellets of the blends were heat-treated for different temperatures between 860°C and 920°C, at times from 1 to 8 hours. The heating rate was 10°C/min., and the cooling rate was 5°C/ min., in an air atmosphere. The pellets were ground and the phase evolution was followed by means of powder XRD.

The sintering behaviour was studied on isopressed samples prepared from $Y_1Ba_2Cu_3O_x$ powder, synthesized at the optimum temperature and time, as determined in the kinetic study. Density measurements, XRD patterns, and reflexion optical microscopy (ROM) with polarized light were obtained on sintered bodies. The sintering process was developed in the 920-940°C temperature range, with times varying between 1 and 8 hours. The heating rate was 3°C/ min., and the cooling rate was 1°C/ min. The cooling cycle was carried out in air atmosphere. Oxygen annealing of sintered samples was not performed in any case.

Transition temperature, T_c, was determined on the synthesized powders by magnetic susceptibility measurements performed on a force magnetometer.

3. RESULTS

The XRD patterns of the barium-yttrium compounds showed the formation of the pure compounds BaY_2O_4 and $Ba_3Y_4O_9$, respectively. No trace of $BaCO_3$ was observed. The XRD of the barium-copper blend showed the formation of $BaCuO_2$, which coexists with uncombined CuO, in a very homogeneous mixture. Only small amounts of liquid were observed in these oxide mixtures. $BaCu_2O_3$ was the nominal composition of the barium-copper-oxide combination.

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The studied reaction sequences were as follows:

$$BaY_2O_4 + 3BaCu_2O_3 \longrightarrow 2Y_1Ba_2Cu_3O_x \quad \text{(Route 1)} \quad [3]$$

$$Ba_3Y_4O_9 + 5BaCu_2O_3 + 2CuO \longrightarrow 4Y_1Ba_2Cu_3O_x \quad \text{(Route 2).} \quad [4]$$

Figure 1 shows the XRD patterns of the samples synthesized according to Route 1 for different temperatures and times. It can be already seen at 880°C, that the synthesis reaction is very advanced for relatively short treatment times--2 to 4 hours. Some amount of Y_2BaCuO_5 compound, the "green phase, 2-1-1," was observed for the 2-hour treatment, along with small amounts of unreacted $BaCuO_2$ and CuO. The yttrium-barium phase was not detected for this time. Higher times led to the progressive disappearance of these phases, and for 16 hours, the only observed compound was the 1-2-3 phase.

At 900°C for 2 hours, the reaction was almost complete; only very small amounts of $BaCuO_2$ could be detected. Beyond this time, traces of second phases were not observed from the XRD patterns. Upon raising the temperature, the results were somewhat different. At 920°C for 2 hours, the final product was pure $Y_1Ba_2Cu_3O_x$ compound, but the heat treatment lengthening led to liquid-phase formation, and to the reappearance of small amounts of the green phase. For times of 8 hours or more, the XRD patterns showed a reinforcement of the 0-0-1 peaks, probably due to the preferential growth of crystals, nucleated from the liquid phase. As can be seen from the XRD patterns, the synthesized $Y_1Ba_2Cu_3O_x$ crystallized with an orthorhombic symmetry, type I. Table I shows the lattice parameters for the three temperatures studied at the 2-hour point. According to the calculated values of lattice parameters, the O_2 content can be evaluated as 6.95. The onset temperature was 91 K for the powder synthesized at 900°C for 2 hours, and slightly varies with temperature and time.

TABLE I

Lattice parameters (in Å) and onset temperature (in K) of powders from Route 1

Reaction synthesis	a_o	b_o	c_o	σ*	Onset temperature
880°C 2h	3.8314	3.8897	11.657	1.51	90
900°C 2h	3.8261	3.8957	11.688	1.80	91
920°C 2h	3.8297	3.8949	11.688	1.69	90

$$*\sigma = 2 \times \frac{b_o - a_o}{b_o + a_o} \times 100 \quad \text{(orthorhombicity parameter)}$$

Figure 2 shows the phase evolution during the heat treatment of the powders corresponding to Route 2. A different behaviour as compared with Route 1 can be observed. The green phase, which is formed in the first state of the synthesis reaction does not disappear totally through the whole heat treatment study. Along with this phase, CuO and $BaCuO_2$ traces are also present. Nevertheless, no appreciable amount of the green phase for the higher temperatures and times was observed. Preferential growth of the synthesized powders is also seen in the samples heated at 920°C for 4 and 8 hours. The $Y_1Ba_2Cu_3O_x$ synthesized by Route 2 also shows an orthorhombic symmetry, type I, with the lattice parameters given in Table II. The onset temperature was 89 K for the powder obtained at 900°C, 2h.

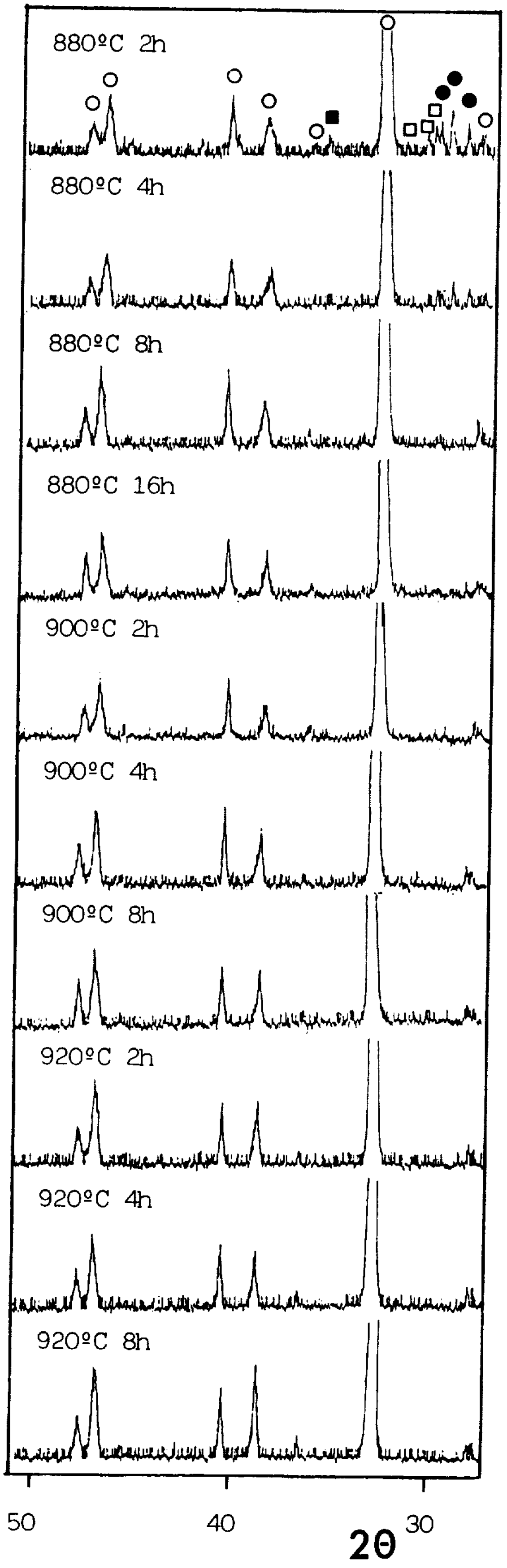

Figure 1. XRD patterns of Route 1, samples heated for different temperatures and times. o $Y_1Ba_2Cu_3$; □ Y_2BaCuO_5; ● $BaCuO_2$; and ■ CuO.

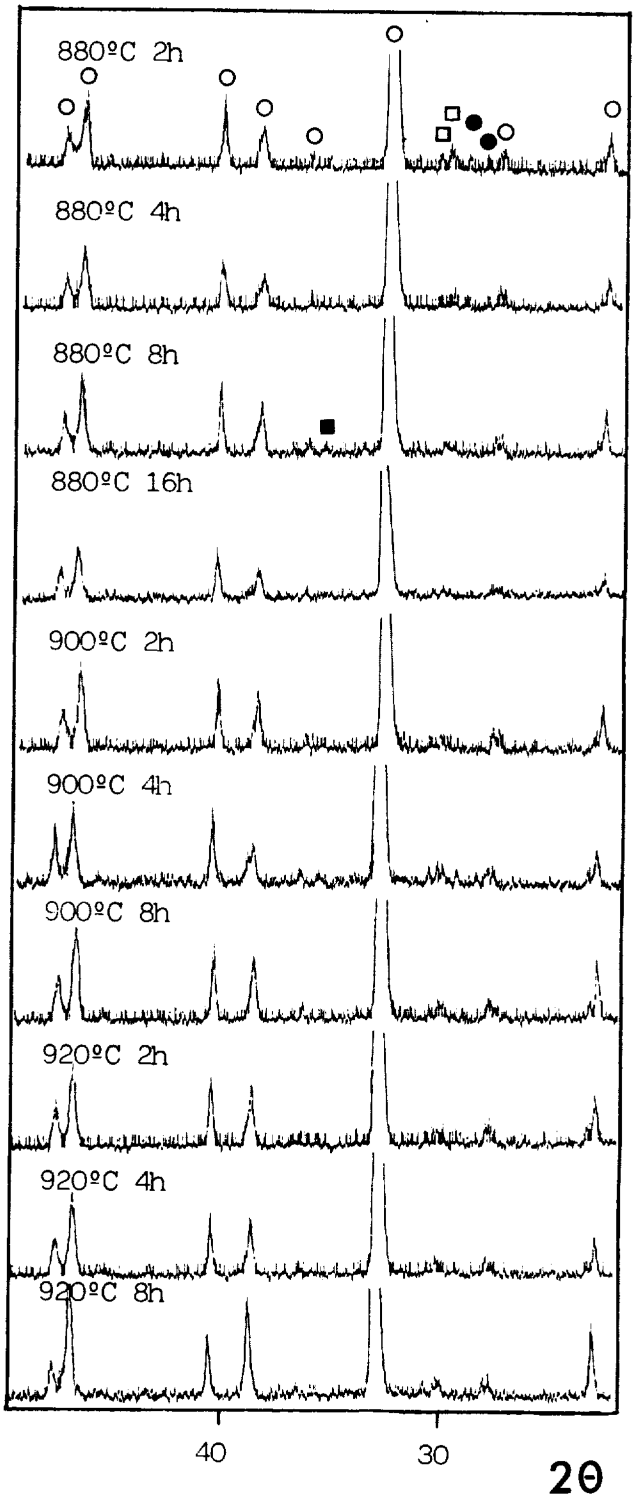

Figure 2. XRD patterns of Route 2 samples heated for different temperatures and times. ■ CuO; o $YBa_2Cu_3O_x$; □ Y_2BaCuO_5; and ● $BaCuO_2$.

TABLE II

Lattice parameters (in Å) and onset temperature (in K) of powders from Route 2

Reaction synthesis	a_o	b_o	c_o	σ	Onset temperature
880°C 2 h	3.8261	3.8956	11.689	1.80	89
900°C 2 h	3.8265	3.8977	11.691	1.84	89
920°C 2 h	3.8245	3.8953	11.691	1.83	88

According to these results, the 900°C, 2-hour schedule was chosen as the better one to obtain synthesis powders for a sintering study. The powders were ball- and attrition-milled, isopressed, and then sintered at different temperatures and times between 920 and 940°C for 1 to 8 hours.

Figure 3 shows the densification curves against temperatures and times for the two synthesis powders. It can be seen that the powder obtained by Route 2 has the best sintering behaviour. It attained a density value of 6.01 gr/cm^3 for 930°C, at 2 hours. By raising the temperature and/or time, somewhat lower density values were attained, but the variation is very smooth. On the other hand, the higher density value for powder synthesized by Route 1 was attained at 940°C for 2 hours, and the value was 5.95 gr/cm^3; smaller than that corresponding to powder 2.

Another important difference between the two materials was the final microstructure and crystal structure. Figure 4 shows ROM micrographs of polished and optically etched, sintered samples. The etching was performed by means of polarized light and crossing nichols. The sample surfaces were not etched by thermal or chemical methods. It can be seen that whereas sample 1 has developed a rather large-grained microstructure with extensive porosity and heavily twinned grains, sample 2 has developed a fine-grained microstructure with scarce porosity and no twinned grains.

The crystal structure of the sintered samples of Route 1 is orthorhombic, with lattice parameters which are in good accordance with type I, as are the synthesis powders. On the other hand, the crystal structure of the sintered samples of Route 2 showed tetragonal symmetry, with lattice parameters which indicated an oxygen content only a little higher than 6.

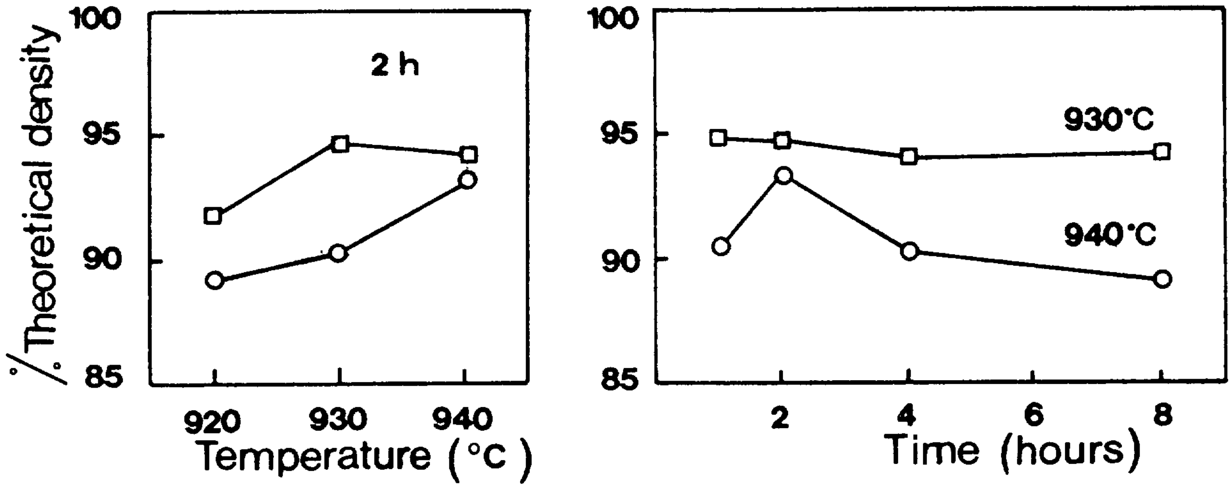

Figure 3. Densification versus sintering temperature and time. o Route 1; □Route 2.

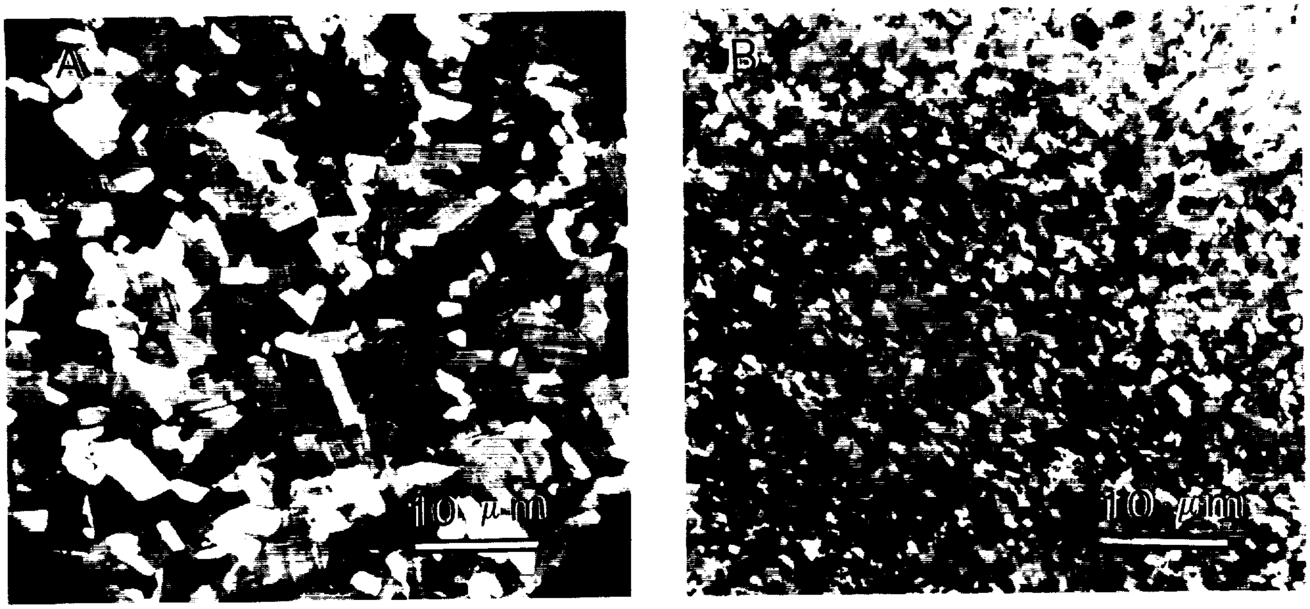

Figure 4. Micrographs of sintered samples: A) Route 1 (940°C); B) Route 2 (930°C)--both for 2 hours.

4. DISCUSSION

$BaCO_3$ has been used as the most reliable source of barium in the forming of $Y_1Ba_2Cu_3O_x$ compound when the solid-state reaction procedure is followed, but as was pointed out above, the sluggish decomposition of the carbonate constitutes a limiting factor in the $Y_1Ba_2Cu_3O_x$ formation. The previous reaction of $BaCO_3$ with Y_2O_3 and/or CuO can avoid this limitation.

The reaction between Y_2BaO_4 and $BaCuO_3$ is very fast and it is possible to obtain pure $Y_1Ba_2Cu_3O_x$ at 900°C for short times; ≤ 2 hours. The low temperature for which the reaction is accomplished can be attributed to the presence of the free CuO which is intimately mixed with $BaCuO_2$. The reaction sequence is likely to occur according to the following scheme:

$$3BaCuO_3 + Y_2BaO_4 \text{ ---- } 2Y_1Ba_2Cu_3O_x \qquad [5] \text{ as major reaction}$$

$$CuO + Y_2BaO_4 \text{ ---- } Y_2BaCuO_5 \qquad [6]$$

$$Y_2BaCuO_5 + 3BaCuO_2 + 2CuO \text{ ---- } 2Y_1Ba_2Cu_3O_x. \qquad [7]$$

[6], [7] as secondary reactions

In this case, the consumption of the green phase is very fast, contrary to the results of Ruckenstein et al. (10), when they studied the reaction shown in eq. 7. The reaction between $Y_4Ba_3O_9$, $BaCu_2O_3$ and CuO is also very fast, probably for the same reasons as those in the first case. The reaction sequence is likely the following:

$$Y_4Ba_3O_9 + 5BaCu_2O_3 + 2CuO \text{ ---- } 4Y_1Ba_2Cu_3O_x \qquad [8] \text{ as major reaction}$$

$$Y_4Ba_3O_9 + 3CuO \text{ ---- } 2Y_2BaCuO_5 + BaCuO_2 \qquad [9]$$

$$Y_2BaCuO_5 + 3BaCuO_2 + 2CuO \text{ ---- } 2Y_1Ba_2Cu_3O_x \qquad [10]$$

[9], [10] as secondary reactions

The lack of reaction completeness in the route could be attributed to the instability of the $Y_4Ba_3O_9$ compound, which is the reaction that occurs with the presence of carbonated phases. We think that the results will improve with a striking control of the synthesis procedure and subsequent storage and handling.

The powder from Route 1 shows a sintering behaviour which indicates liquid phase formation with a considerable grain growth. This liquid has been attributed to the reaction with atmospheric carbon dioxide (13) that forms an oxycarbonate which lowers the liquid formation temperature. The interconnected porosity allows the grain boundary diffusion of oxygen to form an orthorhombic material. The grain size is, moreover, small enough to lead to a complete grain oxygenation (Fig. 4).

Powder 2 has a quite different sintering behaviour. This might be explained by the presence of the minor amounts of the green phase. According to the phase diagram, no liquid formation will occur through the sintering process in the studied temperature range, because of the presence of green phase. As a consequence, controlled grain growth takes place, and therefore, it is possible to obtain better densification values (14). Shaw et al. (15) found that small-grained microstructures with high grain-boundary densities favour the oxygenation of the bulk sintered materials, and make the tetragonal-orthorhombic transition easier. In the present case, small grain size could allow the correct oxygenation, but the presence of the second phase in the grain boundaries forms a barrier to the oxygen diffusion, which explains maintenance of the tetragonal symmetry during the slow cooling to room temperature.

4. CONCLUSIONS

Two procedures have been studied for overcoming the presence of $BaCO_3$ during the solid-state reaction of oxides to obtain $Y_2Ba_2Cu_3O_x$. The procedures allow $Y_1Ba_2Cu_3O_x$ synthesis at low temperatures of 900°C, and times of 2 hours, by means of a single-step process. These temperatures and times are well below the eutetic temperature, and therefore, it is possible to avoid particle growth and to maintain a narrow particle size distribution in the synthesized powders.

The effectiveness of the procedures strongly depends on the stability and reliability of the intermediate phases. The Y_2BaO_9 compound fulfills these conditions. On the other hand, $Y_4Ba_3O_9$ is very unstable in moist air, and partially recarbonates if adequate handling care is not taken. Nevertheless, the procedures based on both compounds have led us to obtain superconducting powders through a single cooling cycle in air beyond the synthesis temperature.

The sintering of these powders gives density values near or higher than 95% D_{th}. The presence of small amounts of green phase allows grain size control and higher densities, but the oxygenation process during cooling is hindered by the presence of that second phase. Without green phase development, $Y_1Ba_2Cu_3O_x$ compound superconducts after sintering without a special oxygen treatment.

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