JOURNAL OF SOLID STATE CHEMISTRY 112, 406–411 (1994)

Differences between the Forming Processes of $RBa_2Cu_3O_{7-x}$ (R = Y, Yb) Phases and Preparation of the Single-Phase Yb-123 Superconductor

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Received July 26, 1993; in revised form January 3, 1994; accepted January 5, 1994

The formation of $YBa_2Cu_3O_{7-x}$ (Y-123) and $YbBa_2Cu_3O_{7-x}$ (Yb-123) phases, the synthesis of single-phase Yb-123, and the lowest temperature for obtaining the single-phase Y-123 superconductor have been studied by X-ray diffraction, differential thermal analysis, and superconductivity measurements. The results indicate that the Y-123 phase is formed from the principle chemical reaction

$$Y_2O_3 + 4BaCO_3 + 6CuO + (1 - 2x)/2O_2 \rightarrow 2YBa_2Cu_3O_{7-x} + 4CO_2\uparrow.$$

The reactions for forming Yb-123 phase are

$$Yb_2O_3 + BaCO_3 + CuO \rightarrow Yb_2BaCuO_5 + CO_2\uparrow$$

$$BaCO_3 + CuO \rightarrow BaCuO_2 + CO_2\uparrow$$

$$Yb_2BaCuO_5 + 3BaCuO_2 + 2CuO + (1 - 2x)/2O_2 \rightarrow 2YbBa_2Cu_3O_{7-x}.$$

In our experiments, the lowest temperature for obtaining the near-single-phase Y-123 bulk superconductor is 780°C; a simple procedure for synthesis of the single-phase Yb-123 superconductor is described.

INTRODUCTION

This first occurrence of superconductivity above the boiling point of liquid nitrogen was reported for the compound $YBa_2Cu_3O_{7-x}$ (Y-123) (1, 2). Substitution of other rare earth elements for Yttrium followed soon thereafter (3–5). Compounds of the general formula $RBa_2Cu_3O_{7-x}$ (R-123) (R = rare earth elements or Y) can be formed except for R = Ce and Tb; however, some of them are difficult to obtain the single phase $R-123$ for when R = Yb, Lu (6–11). For R = Yb, Yb_2BaCuO_5 always exists as an impurity in the $YbBa_2Cu_3O_{7-x}$ (Yb-123) superconductor prepared by the conventional high-temperature ceramic technique, while the single-phase Y-123 is easily obtained. This is attributed to the smaller atom radius of Yb compared to other rare earth atoms, which may cause the relative instability of Yb-123. Much research has been done to reduce the instability of Yb-123 through partly replacing the Ba site with other small atoms or by preparing samples with nonstoichiometric starting materials for hindering the formation of Yb-211. To obtain single-phase Yb-123, Badri and Varadaraju (11) attempted to achieve single-phase formation by partly substituting Sr at the Ba site in Yb-123. This is expected to reduce the instability of Yb-123 by inducing a contraction of the unit cell through replacement of Ba by Sr. These authors obtained single-phase $YbBa_{2-x}Sr_xCu_3O_{7-x}$ (x = 0.1–0.5). However, it is not single-phase Yb-123. Somasundaram *et al.* (12) used an 8% excess CuO to suppress the formation of the Yb-211 phase and obtained a sample with $T_{c(0)}$ = 89 K; however, some CuO impurity was still present.

In the present study, we attempt to compare the formation process of Yb-123 with those of other rare earth elements, and we chose yttrium as an example. Through such a comparison the cause which leads to different results is expected to be found, and the single-phase formation is expected to be achieved by overcoming the difficulties associated with the incomplete formation of Yb-123 during the normal solid-state reaction. We also investigated the lowest temperature for formation of Y-123.

2. EXPERIMENTS

The standard four-probe method is used for superconductivity measurements. X-ray diffraction (XRD) patterns were recorded by a Rigaku Dmax/ra diffractometer using Cu$K\alpha$ radiation. The differential thermal analysis (DTA) measurements were carried out with a CR-G-type apparatus; $\alpha - Al_2O_3$ powder was used as the reference. Finax and Lazy programs are used for the phase identification and for the calculation of lattice parameters.

0022-4596/94 $6.00

3. RESULTS AND DISCUSSIONS

3.1. DTA Experiments of Y_2O_3, Yb_2O_3, $BaCO_3$, and CuO and the Stoichiometric Mixtures of $YO_{1.5}(YbO_{1.5})/BaCO_3/CuO$ = 1:2:3

In order to investigate the formation processes of Y-123 and Yb-123, DTA was carried out for the starting materials and stoichiometric mixture Yb-123, with a heating and cooling rate of 10°C/min. From the weight loss of samples after and before the experiment, the percentage of decomposed $BaCO_3$ was calculated.

The results show that Y_2O_3 and Yb_2O_3 do not exhibit any phase transition below 1300°C. CuO has no phase transition below 900°C.

$$\alpha - BaCO_3 \overset{780°C}{\rightleftharpoons} \beta - BaCO_3 \overset{965°C}{\rightleftharpoons} \gamma - BaCO_3 \rightarrow BaO + CO_2\uparrow$$

For α – $BaCO_3$, a = 0.5314 nm, b = 0.8904 nm, and c = 0.6430 nm, with space group D_{2h}^{16} – $Pmnm$ (JCPDS 5-378). For γ – $BaCO_3$, a = 0.6959 nm, with space group $Fm3m$ (11-697).

$BaCO_3$ has two phase transitions below 1000°C, and γ – $BaCO_3$ begins to decompose at 1160°C, which is complete at 1350°C. In the Yb-123 mixture, the phase transition and decomposition temperatures of $BaCO_3$ are lowered because of the coexistence of Yb_2O_3 and CuO.

3.2. Forming Processes of the Y-123 and Yb-123 Phases

In order to compare the formation process of Y-123 with that of Yb-123, stoichiometric Y Yb-123 mixtures were mixed, ground throughly, pressed into pellets, and placed into a Pt crucible. The samples were respectively sintered for 30 hr at 300, 400, 500, 600, 650, 700, 735, 770, 800, 820, and 850 ±5°C under the same heating schedule (heating and cooling rates are 75°C/hr and 30°C/hr, respectively). The Y Yb-123 phase formation processes were investigated according to the variations of sample weight, phase, and superconductivity after and before every sintering process.

These experiments show that Y_2O_3, Yb_2O_3, and CuO do not suffer any weight loss below 900°C; therefore the weight loss of the samples is due to the decomposition of $BaCO_3$. Because the amount of $RBa_2Cu_3O_{7-x}$ formed from decomposition of $BaCO_3$ and oxygen content (x) changes with sintering temperature, the amount of decomposed $BaCO_3$ is not easily determined accurately. It is found that the weight of the sample sintered at 820°C did not change after a further heating process at 850°C for 30 hr; therefore, we state that the loss weight due to $BaCO_3$ decomposition is $M = M_0 - M_{850}$, where M_0 is the weight of the starting sample, and M_{850} represents the weight of sample after sintering at 850°C for 30 hr. The precentage (P_T) of decomposed $BaCO_3$ sintered at each temperature is

$$P_T = \frac{M_0 - M_T}{M_0 - M_{850}} \times 100\%.$$

Figure 1 shows the T_c of samples and the relation between percentage of decomposed $BaCO_3$(P_T) and sintering temperature. When the sintering temperature is below 650°C, the weight of the Y Yb-123 stoichiometric mixture did not change, and the samples sintered at this temperature did not exhibit superconductivity. The Y-123 sample sintered at 700°C for 30 hr began to exhibit superconductivity; this means that the superconductive phase was formed. When the sample loses some weight, this indicates that the decomposition of $BaCO_3$ and the formation of Y-123 are interlinked. As the temperature is increased further, more $BaCO_3$ is decomposed and more Y-123 is formed. When the temperature is raised to 820°C, almost all $BaCO_3$ is decomposed and the T_c of the sample increases to 92 K. For Yb-123, samples did not exhibit any superconductivity until the sintering temperature was raised to 800°C. In other words, when the temperature remains below 800°C the decomposition of $BaCO_3$ does not lead to the formation of Yb-123.

Comparing Y-123 with Yb-123, as long as the temperature is below 800°C, the decomposition of $BaCO_3$ is similiar (Fig. 1); however, one leads to the formation of the superconductive phase, but the other does not.

The XRD patterns of Y-123 and Yb-123 mixtures samples sintered at different temperatures are shown in Fig. 2 and Fig. 3, respectively. Markers are used to indicate each phase obtained at different temperatures. All phases that existed in samples heated at different temperatures are listed in Table 1.

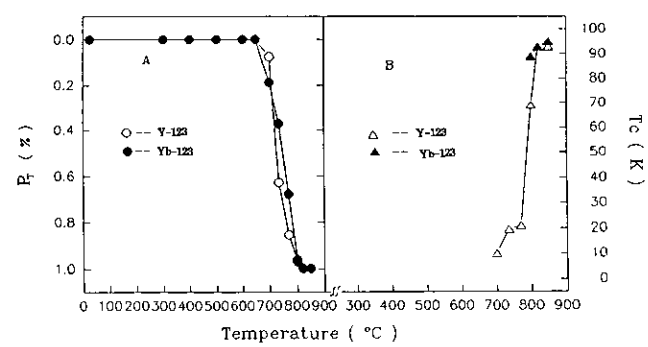

FIG. 1. (A) The percentage of decomposed $BaCO_3$ in Y(Yb)-123 mixture vs sintering temperature. (B) The relation between superconductivity of samples and sintering temperature. △, ○, Y-123 mixture; ▲, ●, Yb-123 mixture.

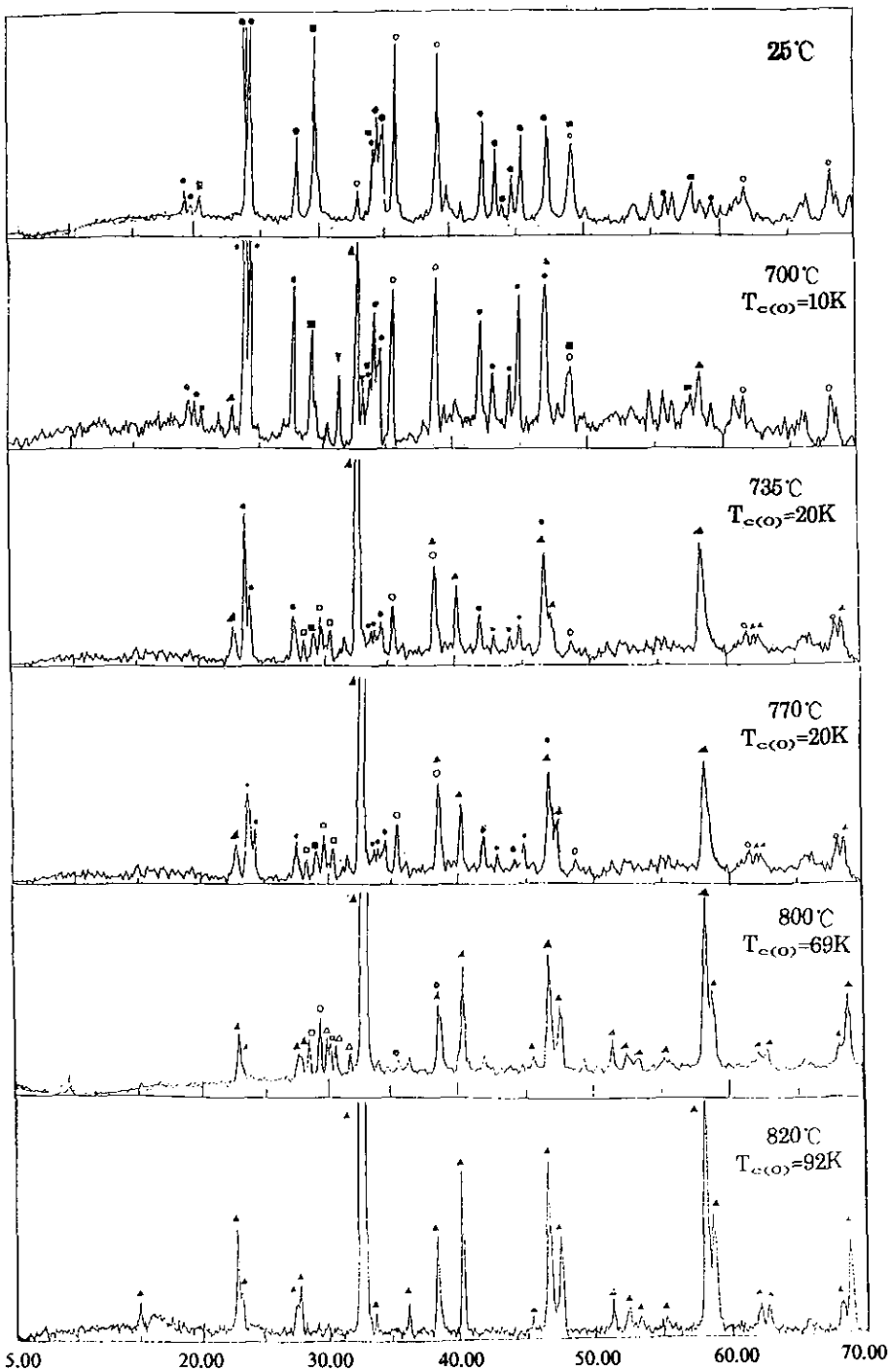

FIG. 2. The XRD patterns of the Y-123 mixture sintered at different temperatures. ●, $BaCO_3$; ■, Y_2O_3; ○, CuO; ▲, Y-123; ▼, $Y_2Cu_2O_5$; □, $BaCuO_2$; △, Y-211.

It can bee seen from Table 1 and Fig. 2 that the Y-123 phase begins to form at 700°C; as the temperature is increased further, more superconducting material is obtained, and the superconducting transition temperature T_c becomes higher. Single-phase Y-123 with T_c = 92 K is formed at 820°C. The phase identifications in Table 1 and Fig. 2 indicate that the Y-123 phase is formed by the main chemical reaction

$$Y_2O_3 + 4BaCO_3 + 6CuO + (1 - 2x)/2O_2 \rightarrow 2YBa_2Cu_3O_{7-x} + 4CO_2\uparrow .$$

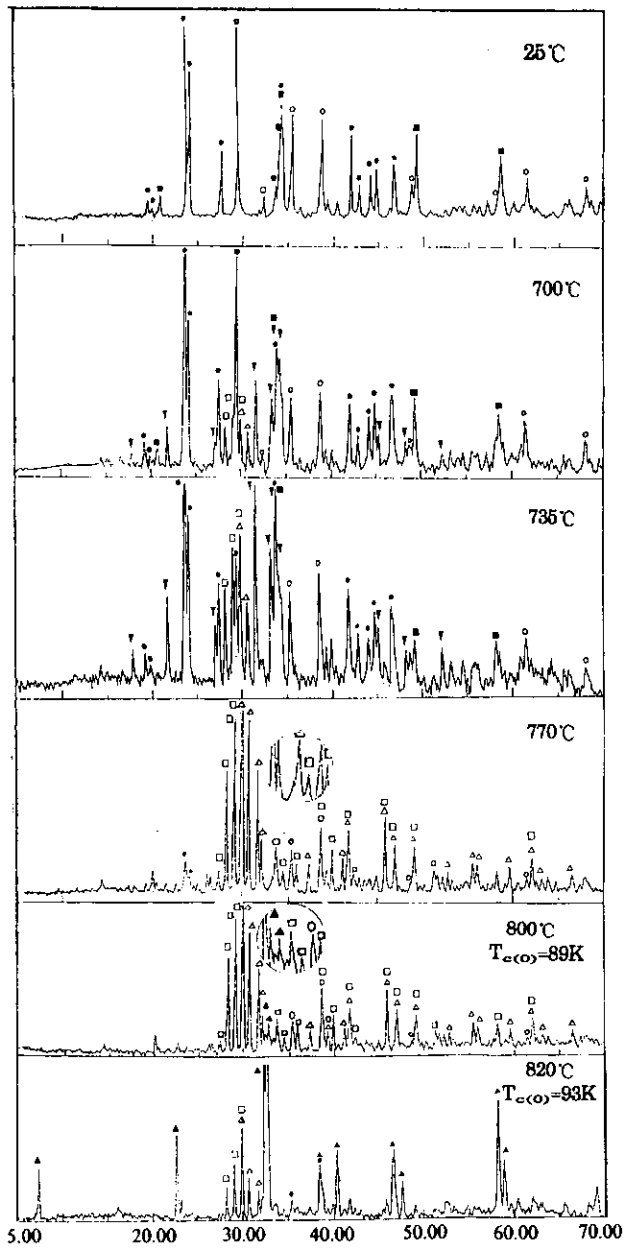

FIG. 3. The XRD patterns of the Yb-123 mixture sintered at different temperatures. ●, $BaCO_3$; ■, Yb_2O_3; O, CuO; ▲, Yb-123; ▼, $Yb_2Cu_2O_5$; □, $BaCuO_2$; △, Yb-211.

It is seen from Fig. 3 and Table 1 that the formation of Yb-123 is essentially different from that of Y-123. When the temperature increases to 700°C, Yb-123 is not formed as is Y-123; however, the $BaCO_3$ in the sample begins to decompose. As the temperature is raised to 770°C, most of the $BaCO_3$ in the sample is decomposed, and this process does not lead to formation of Yb-123. In all processes, Yb-211 and $BaCuO_2$ are obtained as the main phases through the chemical reactions

$$Yb_2O_3 + BaCO_3 + CuO \rightarrow Yb_2BaCuO_5(\text{Yb-211}) + CO_2\uparrow \; BaCO_3 + CuO \rightarrow BaCuO_2 + CO_2\uparrow.$$

When the temperature increases to 800°C, the sample begins to exhibit superconductivity, which indicates that Yb-123 is formed. The Yb-123 phase is clearly seen in the enlarged section of Fig. 3. When the temperature increases further, a great quantity of Yb-211 and $BaCuO_2$ transforms into Yb-123 according to the reaction

$$Yb_2BaCuO_5 + 3BaCuO_2 + 2CuO + (1 - 2x)/2O_2 \rightarrow 2YbBa_2Cu_3O_{7-x}.$$

The formation processes of Y-123 and Yb-123 are different, although they have the same structure and exhibit similiar superconducting properties. The difference may arise from the greater stability of Yb-211 (9). Compared to Y-211, it is easier to form Yb-211 at relatively low temperatures. As the temperature is increased, Yb-211 transforms into Yb-123. The difference between the formation processes of Yb-123 and Y-123 shows that single-phase Yb-123 is more difficult to obtain, using the same method as that for Y-123.

3.3. Synthesis of the Single-Phase Yb-123 Superconductor

In order to find the optimum temperature for sintering Yb-123, we investigated the relation between the formation of Yb-123 and the sintering temperature. The starting mixture of stoichiometric Yb-123 was throughly mixed, ground, pressed into pellets, and then sintered at 800, 820, 830, 850, and 880°C, respectively, for 30 hr. The Yb-

TABLE 1
The Phases in the Y(Yb)-123 Mixture Samples Sintered at Different Temperatures

Sintering temperature (°C)	Phase	
	Y-system samples	Yb-system samples
25	Y_2O_3 (Y), $BaCO_3$ (B), CuO (C)	Yb_2O_3 (Yb), $BaCO_3$ (B), CuO (C)
700	Y, B, C, Y-123, $Y_2Cu_2O_5$	Yb, B, C, $BaCuO_2$ (BC), Yb-211, $Yb_2Cu_2O_5$
735	Y-123, Y, B, C, $BaCuO_2$ (BC)	Yb, B. C, Yb-211, BC, $Yb_2Cu_2O_5$
770	Y-123, Y, B, C, BC	B, C, Yb-211, BC
800	Y-123, BC, C, Y-211	Yb-211, BC, Yb-123, C
820	Y-123	Yb-123, Yb-211, BC, C

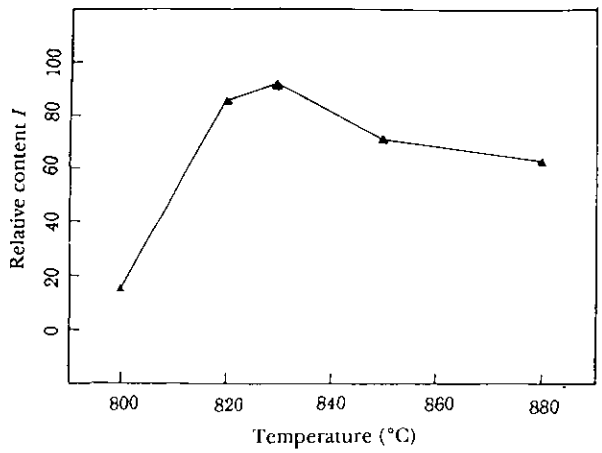

FIG. 4. The relative content of the Yb-123 phase in sample vs sintering temperature.

123 content in the samples was determined by XRD. The relative content of Yb-123 is represented by I,

$$I = \frac{I_{103}(\text{Yb-123})}{I_{103}(\text{Yb-123}) + I_{131}(\text{Yb-211})} \times 100\%,$$

where I_{103}(Yb-123) and I_{131}(Yb-211) represent respectively the intensities of the (103) and (131) diffraction lines of Yb-123 and Yb-211. The results are shown in Fig. 4. It can be seen that the relative content of Yb-123 increases with increasing temperature; however, when temperature is increased further, the relative content of Yb-123 decreases. Single-phase Yb-123 cannot be obtained by just increasing the sintering temperature; this is in agreement with results cited in the literature (10). The optimum temperature range is 820–830°C for transforming Yb-123 and $BaCuO_2$ into Yb-123. On the basis of these results, we reground the samples sintered at 820°C for 30 hr, pressed them into pellets, and sintered them twice under the same conditions. The single-phase Yb-123 superconductor with T_c = 92 K was then obtained. Its XRD pattern is shown in Fig. 5. The lattice parameters obtained for Yb-123 are a = 0.3796, b = 0.3873, and c = 1.1671 nm. In all preparation processes, regrinding and reheating for several times are necessary for formation of single-phase Yb-123. These findings are similar to the results published in the literature (14); however, the sintered temperature used in our experiments is relatively low. One should note that high temperatures are disadvantageous to the formation of single-phase Yb-123.

3.4. The Lowest Sintering Temperature for Forming the Y-123 Superconductor

Since the formation temperature of Y-123 depends on the heating rate and holding time, we tried to find the lowest sintering temperature for forming single-phase Y-123. This information is useful for preparing wire and ribbon material superconductors. The lowest temperature for forming Y-123 is 700°C, as mentioned above. At this temperature, samples must be sintered for a long time, but single-phase Y-123 cannot be obtained. We gradually raised the sintering temperature and reground samples twice. The sample sintered at 780°C for 60 hr exhibits near-single-phase Y-123 with T_c = 93 K. The XRD pattern is shown in Fig. 6; Its lattice parameters are a = 0.3824, b = 0.3862, c = 1.1714 nm.

4. CONCLUSION

The formation process of Yb-123 is different form that of Y-123, which is formed directly from the starting materials. Yb-123, Yb-211, and $BaCuO_2$ are formed at rela-

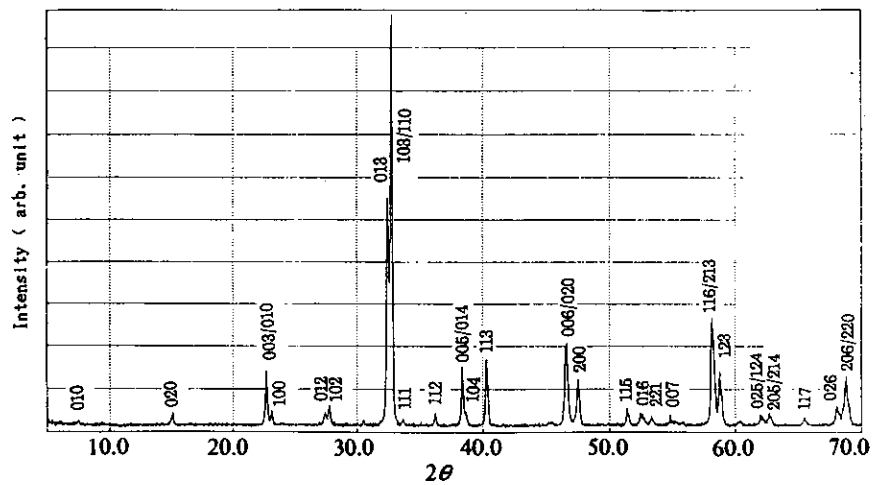

FIG. 5. The XRD pattern of the single-phase Yb-123 sample.

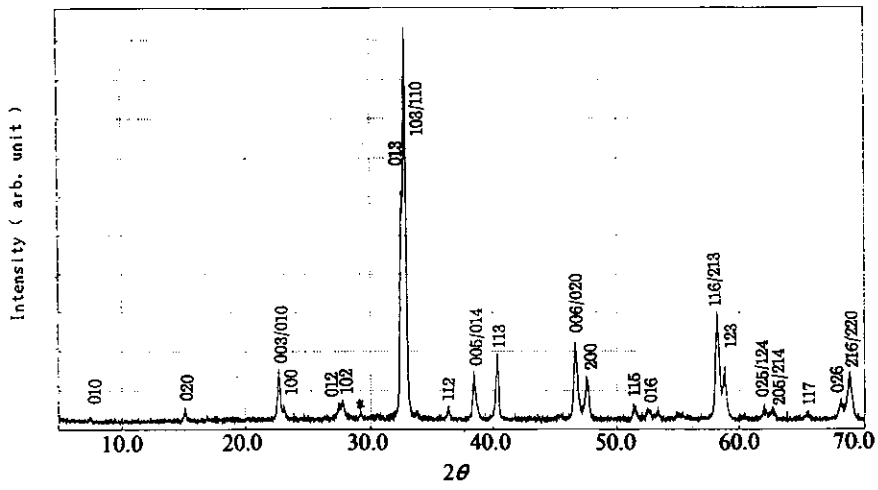

FIG. 6. The XRD pattern of the near-single-phase Y-123 sample with $T_c(0)$ = 92 K obtained at 780°C (*, impurity phase).

tively low sintering temperatures and then transform into Yb-123 at 800°C. A simple method to prepare single-phase Yb-123 has been found. In our experiments, the lowest temperature of formation of near-single-phase Y-123 is 780°C.

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