

## Reaction mechanism in non-isothermal synthesis of high- $T_c$ superconducting oxide $\text{YBa}_2\text{Cu}_3\text{O}_7$

Nae-Lih Wu and Ying-Chih Chang

*Department of Chemical Engineering, National Taiwan University, Taipei (Taiwan)*

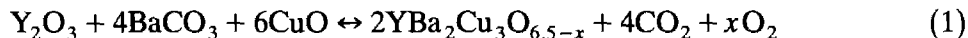
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### Abstract

The reaction mechanism taking place in the non-isothermal synthesis of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  from a mixture containing stoichiometric amounts of  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$  and  $\text{CuO}$  at constant heating rates, ranging from 1 to  $10^\circ\text{C min}^{-1}$ , was investigated by using thermal and X-ray diffraction analyses. It was found that, prior to  $\text{YBa}_2\text{Cu}_3\text{O}_7$  formation,  $\text{Y}_2\text{O}_3$  reacted extensively with  $\text{CuO}$  to form  $\text{Y}_2\text{Cu}_2\text{O}_5$  between 820 and  $920^\circ\text{C}$ , and that thermal analysis using  $\text{Y}_2\text{Cu}_2\text{O}_5$  as the source of yttrium showed the same DTA peak at  $960^\circ\text{C}$  for  $\text{YBa}_2\text{Cu}_3\text{O}_7$  formation as when  $\text{Y}_2\text{O}_3$  is used. Thermal analysis of the various possible reactions involving the decomposition of  $\text{BaCO}_3$  suggested that formation of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  within this peak mainly followed the reaction pathway consisting of  $\text{BaCO}_3 + \text{CuO} \leftrightarrow \text{BaCuO}_2 + \text{CO}_2$  and  $4\text{BaCuO}_2 + \text{Y}_2\text{Cu}_2\text{O}_5 \leftrightarrow 2\text{YBa}_2\text{Cu}_3\text{O}_7$ , whereas a second reaction pathway consisting of  $\text{Y}_2\text{Cu}_2\text{O}_5 + \text{BaCO}_3 \leftrightarrow \text{Y}_2\text{BaCuO}_5 + \text{CuO} + \text{CO}_2$  and  $\text{Y}_2\text{BaCuO}_5 + 3\text{BaCO}_3 + 5\text{CuO} \leftrightarrow 2\text{YBa}_2\text{Cu}_3\text{O}_7 + 3\text{CO}_2$  also took place but only at temperatures within the tail region of the peak. Melting of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , which gave rise to an additional endothermic peak at  $970^\circ\text{C}$ , occurred for calcinations at high heating rates where  $\text{BaCO}_3$  was not completely consumed within the  $960^\circ\text{C}$  peak region. Controversies over the differing numbers of DTA peaks reported in earlier studies are explained.

### INTRODUCTION

Although the high- $T_c$  superconducting oxide  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , also known as the 123 compound, has been routinely synthesized via the solid state reaction



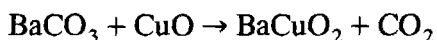
the reaction mechanism involved is not well understood. During the early research following the discovery of this compound, non-isothermal analyses, including DTA (differential thermal analysis) and TGA (thermogravi-

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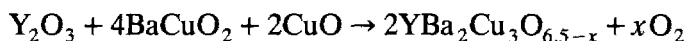
*Correspondence to:* N.-L. Wu, Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan.

Dedicated to Professor Joseph H. Flynn in honour in his 70th birthday.

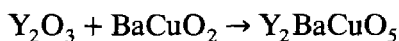
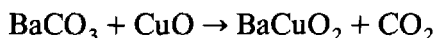
metric analysis), were employed routinely to determine the required calcination temperature for the process (for example, see refs. 1–3) but no information regarding its reaction mechanism has been given. A few studies [4,5] have recently reported both the reaction mechanism and the associated kinetic parameters but their results do not agree with one another. For example, Jiang et al. [4] reported DTA curves with one reaction peak between 900 and 1000°C for reaction (1) and proposed a two-step reaction scheme consisting of



and



However, Gadalla and Hugg [5] reported two DTA peaks over the same temperature range and assigned these peaks to three reaction steps, including



and



In these studies, the reaction mechanisms suggested were based on the compositions of samples subjected to prolonged isothermal heating at a few selected temperatures. It is not reasonable to assume that the compositions thus obtained correspond to those occurring during the DTA analysis, where the samples were heated dynamically at continuously increasing temperatures. Furthermore, none of these studies have conducted thermal analysis on each of the reaction steps proposed in order to check for consistency.

The object of the present study is to re-investigate the reaction mechanism involved in the non-isothermal analysis of reaction (1), with the intention of resolving the controversies presented in the earlier studies. In this work, in addition to the thermal analysis which was conducted over a wider heating-rate range ( $1\text{--}10^\circ\text{C min}^{-1}$ ) than in the earlier studies, XRD analysis was carried out on powders heated at the same heating rates as those in the thermal analysis and quenched from selected temperatures. The powders thus prepared indeed showed different compositions from those reported in the earlier studies and a new reaction mechanism was therefore suggested. The thermal analysis results of the reaction steps involved in the new mechanism were consistent with those obtained from the overall reaction.

## EXPERIMENTAL

To prepare samples for thermal and X-ray diffraction (XRD) analyses, powders of  $\approx 20$  g containing  $Y_2O_3$ ,  $BaCO_3$  and/or  $CuO$  with selected stoichiometries were ground in an automatic agate mortar. For the thermal analysis, the reactant powders were loaded in a platinum cell and heated in a UVAC TGD-7000 at a constant heating rate ranging from 1 to  $10^\circ C \text{ min}^{-1}$  to obtain simultaneous DTA and TG curves, along with their derivatives. A sample size of 280 mg was employed.

For the XRD experiments, the reactant mixtures were calcined in a programmable tubular furnace at constant heating rates as in the thermal analysis. The powders were quenched in air from selected temperatures and ground for XRD analysis to determine their compositions. The XRD patterns were taken in a Regaku D/MAX IIIA diffractometer at a scanning rate of  $2^\circ 2\theta \text{ min}^{-1}$  and 10 wt.% of silver powder was added to the XRD samples to serve as a standard for intensity correction. All the XRD intensities reported in this work are normalized by the intensity of the Ag (200) reflection in the same spectrum.

## RESULTS AND DISCUSSION

For heating at  $1^\circ C \text{ min}^{-1}$  (curve 1 in Fig. 1(a)), two endothermic peaks, at  $\approx 810^\circ C$  and  $\approx 960^\circ C$ , were detected within the range between 800 and  $1000^\circ C$ . The  $810^\circ C$  peak was associated with no weight loss (Fig. 1(b)) and is known to result from the transformation of  $BaCO_3$  from the orthorhombic,  $\gamma$ -phase to the rhombohedral,  $\beta$ -phase. The  $960^\circ C$  peak, however, was accompanied by a large weight loss (Fig. 1(b)) and, as shown by the XRD analysis (see later), was associated with the formation of the 123 compound. The weight change is apparently due to the loss of  $CO_2$  and some  $O_2$ . Furthermore, from the DTG curve (curve 2 in Fig. 1(b)), it was noted that reaction was already proceeding at significant rates between 910 and  $940^\circ C$  before it reached the maximum at  $960^\circ C$ .

When the heating rate was increased to  $2^\circ C \text{ min}^{-1}$  (curve 1 in Fig. 2), an additional endothermic peak occurred at  $970^\circ C$ . (For brevity, the  $960^\circ C$  DTA peak will be referred to hereafter as the LT peak, and the  $970^\circ C$  as the HT peak.) Both LT and HT peaks shifted toward higher temperatures as the heating rate was further increased, but the latter shifted more rapidly than the former (curves 2–4 in Fig. 2). It was also noted that the LT and HT peaks occurred at about the same temperatures as the peaks reported by Gadalla and Hugg [5].

To understand the nature of the LT and HT peaks, XRD studies were conducted to determine the compositions of the partially reacted powders as described in the Experimental section above. For heating at  $1^\circ C \text{ min}^{-1}$  (Fig. 3(a)), the amount of the 123 compound increased steadily with

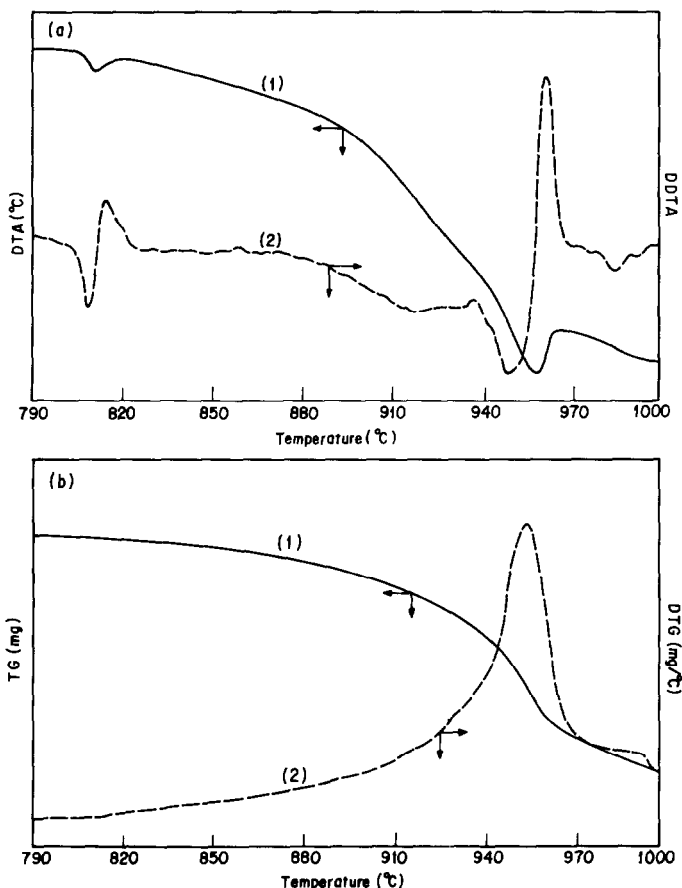


Fig. 1. (a) DTA curve (curve 1) and its derivative (DDTA) (curve 2) for the formation of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  at  $1^\circ\text{C min}^{-1}$ . (b) TG curve (curve 1) and its derivative (DTG) (curve 2) for the formation of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  at  $1^\circ\text{C min}^{-1}$ .

temperature until it was almost completely saturated at  $\approx 960^\circ\text{C}$ . The amount of  $\text{BaCO}_3$ , decreased accordingly with temperature. Because an almost single-phase 123 powder was obtained at  $960^\circ\text{C}$  and because there was only one LT peak between  $850$  and  $960^\circ\text{C}$  on the DTA curve measured at  $1^\circ\text{C min}^{-1}$  (Fig. 1(a)), it is suggested that the LT peak alone is associated with a reaction mechanism leading to the formation of the 123 compound. In addition to the 123 compound,  $\text{Y}_2\text{Cu}_2\text{O}_5$  and  $\text{Y}_2\text{BaCuO}_5$  were also detected (Fig. 3(a)). An appreciable amount of  $\text{Y}_2\text{Cu}_2\text{O}_5$  was present at temperatures as low as  $880^\circ\text{C}$  and it disappeared at  $\approx 950^\circ\text{C}$ .  $\text{Y}_2\text{BaCuO}_5$ , however, began to appear at  $940^\circ\text{C}$  and reached a maximum at  $\approx 950^\circ\text{C}$ .

At a heating rate of  $5^\circ\text{C min}^{-1}$  (Fig. 3(b)) the amount of 123 compound was found to first increase and then decrease with temperature. The maximum XRD intensity of the 123 compound occurred at  $\approx 960^\circ\text{C}$  and was only two-thirds of the saturation intensity measured at  $1^\circ\text{C min}^{-1}$  (Fig.

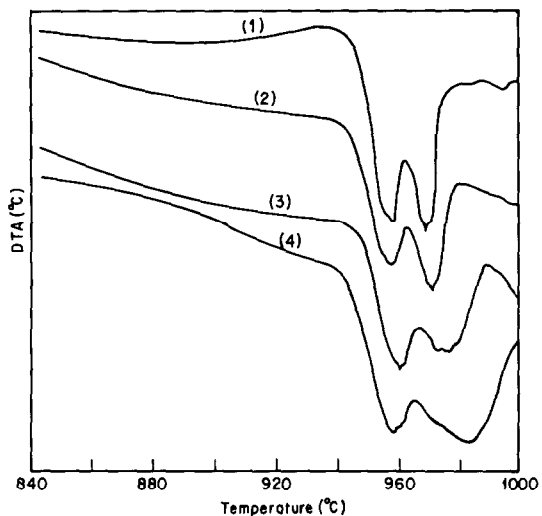


Fig. 2. DTA curves for the formation of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  at: (1)  $2^\circ\text{C min}^{-1}$ ; (2)  $3^\circ\text{C min}^{-1}$ ; (3)  $5^\circ\text{C min}^{-1}$ ; and (4)  $7^\circ\text{C min}^{-1}$ .

3(a)). Immediately following the maximum, a rapid drop in the amount of 123 compound was noted between 965 and 970°C. Comparisons between these XRD data (Fig. 3(b)) and the DTA curves obtained at the same heating rate (Fig. 2) indicate clearly that the increase in the amount of 123 compound below 960°C can be attributed to the reaction mechanism associated with the LT peak and that the HT thermal event does not lead to the formation of 123 compound but to the destruction of already formed 123 compound. In addition to  $\text{Y}_2\text{BaCuO}_5$  and  $\text{Y}_2\text{Cu}_2\text{O}_5$ ,  $\text{BaCuO}_2$  was also detected as a by-product at  $5^\circ\text{C min}^{-1}$ . In particular, it was noted that above 965°C, i.e. at temperatures where the amount of 123 compound decreased, the amounts of  $\text{Y}_2\text{BaCuO}_5$  and  $\text{BaCuO}_2$  increased steadily with temperature, showing no decay in their amounts up to 990°C.

The presence of significant amounts of  $\text{Y}_2\text{Cu}_2\text{O}_5$  at temperatures well below the LT peak (Fig. 3(a) and (b)), e.g. 880°C, suggests the possibility of extensive reaction between  $\text{Y}_2\text{O}_3$  and  $\text{CuO}$  to form  $\text{Y}_2\text{Cu}_2\text{O}_5$  during the course of heating, before formation of the 123 compound commenced within the LT peak. Figure 4 shows the molar ratios of  $\text{Y}_2\text{Cu}_2\text{O}_5$  to the 123 compound, calculated from the XRD intensity data according to Itoh et al. [6], for samples heated at different rates (1 and  $5^\circ\text{C min}^{-1}$ ) versus the quench temperature. It was noted that, while the XRD intensities of  $\text{Y}_2\text{Cu}_2\text{O}_5$  detected in the partially reacted samples were weaker than those of the 123 compound (Fig. 3(a) and (b)), in some cases it is actually present in a larger amount than the 123 compound (Fig. 4). For example, the XRD intensity ratio of  $\text{Y}_2\text{Cu}_2\text{O}_5/123$  in the powder heated at  $1^\circ\text{C min}^{-1}$  and quenched at  $880^\circ\text{C min}^{-1}$  is 1/3. This corresponds to a molar ratio of

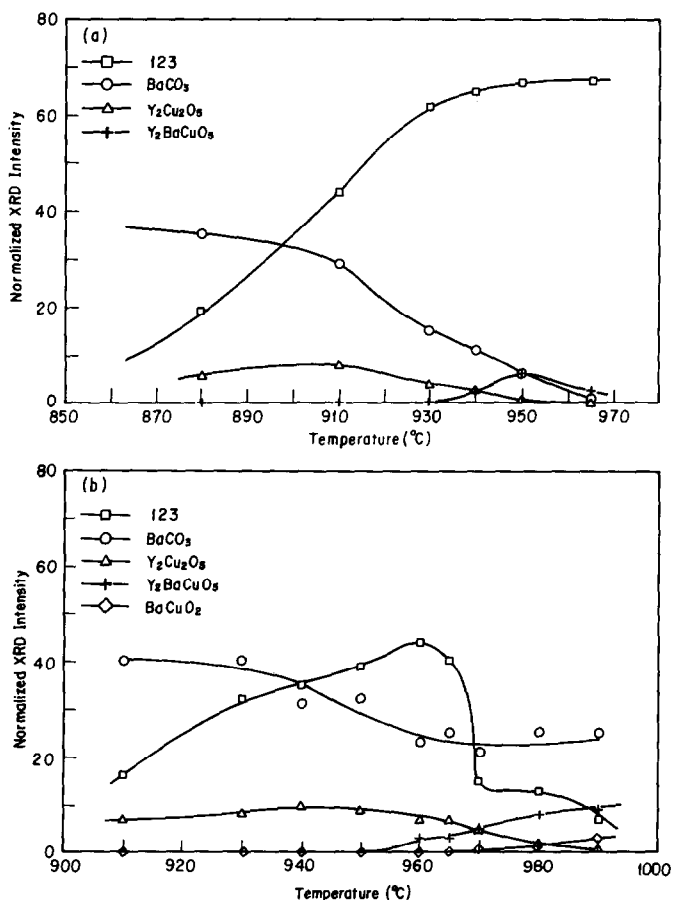


Fig. 3. Normalized XRD intensities vs. quench temperature for reactants and products formed during the course of heating at (a) 1°C min<sup>-1</sup> and (b) 5°C min<sup>-1</sup>. The XRD reflections used in the figures include (110)+(103) for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, (211) for Y<sub>2</sub>Cu<sub>2</sub>O<sub>5</sub>, (311) for Y<sub>2</sub>BaCuO<sub>5</sub>, (600) for BaCuO<sub>2</sub> and (111) for BaCO<sub>3</sub>.

Y<sub>2</sub>Cu<sub>2</sub>O<sub>5</sub>:123 of 1.2:1. Consequently, the reaction between Y<sub>2</sub>O<sub>3</sub> and CuO prior to the formation of the 123 compound should not be overlooked when one interprets the DTA curve of reaction (1).

DTA analysis on the reaction



showed a broad endothermic peak at  $\approx 900^\circ\text{C}$  (curve 1 in Fig. 5). XRD analysis of the sample which had a starting composition of Y<sub>2</sub>O<sub>3</sub>:CuO = 1:2 and was quenched from 910°C indicated that the peak was due to the formation of Y<sub>2</sub>Cu<sub>2</sub>O<sub>5</sub>. Estimation based on the derivative of the DTA curve (DDTA) showed that reaction (2) commenced as low as 820°C and was complete at  $\approx 920^\circ\text{C}$ . This temperature range is well below the LT-peak temperature. Furthermore, it was found that when powders with a

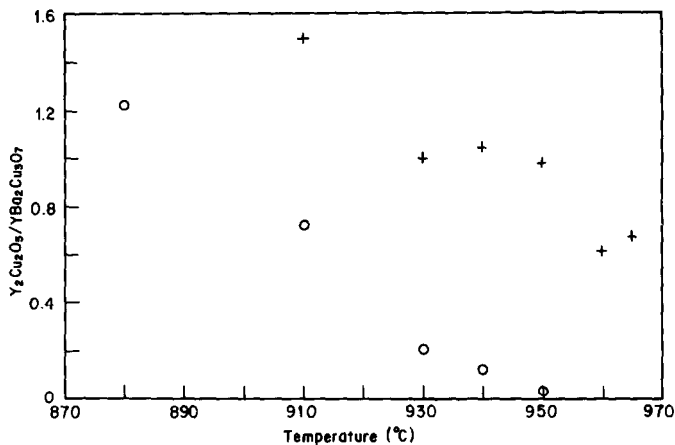


Fig. 4. Molar ratio of  $Y_2Cu_2O_5:YBa_2Cu_3O_7$  vs. quench-temperature for heating at  $1^\circ C \text{ min}^{-1}$  (○) and  $5^\circ C \text{ min}^{-1}$  (+).

composition of  $Y_2Cu_2O_5:BaCO_3:CuO = 0.5:2:2$ , which would eventually produce a single-phase 123 powder, were heated at different rates (curves 2 and 3 in Fig. 5), we obtained the same DTA peaks as the LT and HT peaks detected in the cases where individual  $Y_2O_3$  and CuO were employed (Figs. 1(a) and 2). These results suggested that, due to the extensive reaction between  $Y_2O_3$  and CuO at low temperatures, the formation of the 123 compound within the LT peak can be considered as

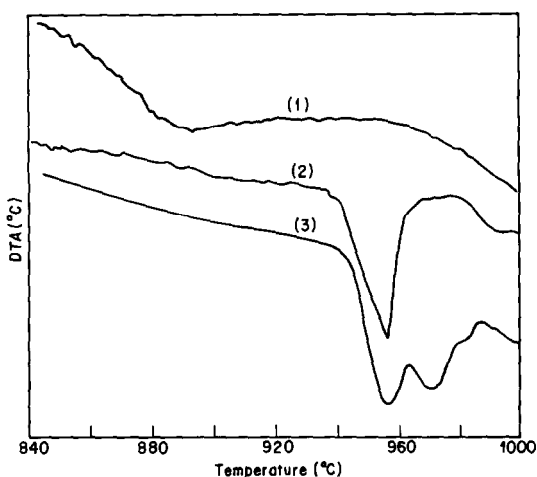
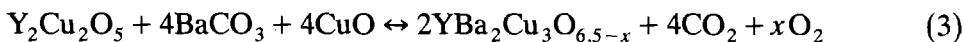


Fig. 5. DTA curves for the formation of (curve 1)  $Y_2Cu_2O_5$  via reaction (2) at  $1^\circ C \text{ min}^{-1}$  and (curves 2 and 3)  $YBa_2Cu_3O_7$  via reaction (3) at 1 and  $5^\circ C \text{ min}^{-1}$ , respectively.

The formation of  $Y_2Cu_2O_5$  during the course of heating was neglected completely in the earlier studies, perhaps due to the fact that the thermal effect caused by the formation of  $Y_2Cu_2O_5$  is much smaller than those of the LT and HT peaks and, as a result, has been unnoticed. For example, when powders of the same weights were employed, the DTA peak intensity for the formation of  $Y_2Cu_2O_5$  from a ( $Y_2O_3 + 2CuO$ ) powder is only one-seventh of the intensity of either the LT or HT peak. Nevertheless, as shown by the DDTA curves of reaction (1) (for example, see curve 2 in Fig. 1(a)), an endothermic event, indicated by a dip in the DDTA curve, did occur near 910°C.

Examination of partially reacted samples of low conversion clearly identified different colors, which suggested different compositions, along the depth of the powder bed. The samples typically consisted of a black top portion and a grayish bottom containing dispersed blue aggregates. XRD studies on the samples sectioned from different portions of the powder bed indicated that the formation of the 123 compound, which is black, took place mainly within the top portion of the bed, while  $Y_2Cu_2O_5$ , which appears blue, occurred preferentially within the bottom portion. For powders heated at  $1^\circ C \text{ min}^{-1}$  and quenched from temperatures above 950°C,  $Y_2BaCuO_5$  also occurred preferentially within the bottom portion which constituted only a very small fraction of the entire powder bed.

The formation of the 123 compound via reaction (1) produced  $CO_2$ . The fact that the 123 compound formed preferentially within the top portion of the powder bed suggested a distribution of the extent of  $BaCO_3$  decomposition along the depth of the powder bed, which is typical of a reversible decomposition reaction. Consider the decomposition of  $BaCO_3$  in a powder bed heated at continuously increased temperatures. As the powder is heated to the temperature where the equilibrium  $CO_2$  pressure of  $BaCO_3$  decomposition exceeds that in the ambient atmosphere,  $CO_2$  is generated via  $BaCO_3$  decomposition. The  $CO_2$  partial pressure within the lower portion of the powder bed is spontaneously raised and  $BaCO_3$  decomposition, and hence the reaction in which it is involved, is retarded therein. The  $CO_2$  generated in the upper portion of the powder diffuses into the ambient atmosphere and the reaction occurs at the upper surface of the powder bed where the  $CO_2$  partial pressure is lower than that in the interior. The front of the decomposition (or reaction) zone moves into the powder bed as heating continues. This explains why the formation of the 123 compound took place preferentially within the top portion of the powder bed. Furthermore, it is also clear that for reactions limited by the removal of  $CO_2$ , the higher the equilibrium  $CO_2$  pressure of the reaction, the lower the temperatures at which the reaction can commence and complete. Based on the peak temperatures of reactions involving decomposition of  $BaCO_3$ , we evaluated possible reaction mechanism(s) for the formation of the 123 compound within the LT region as follows.



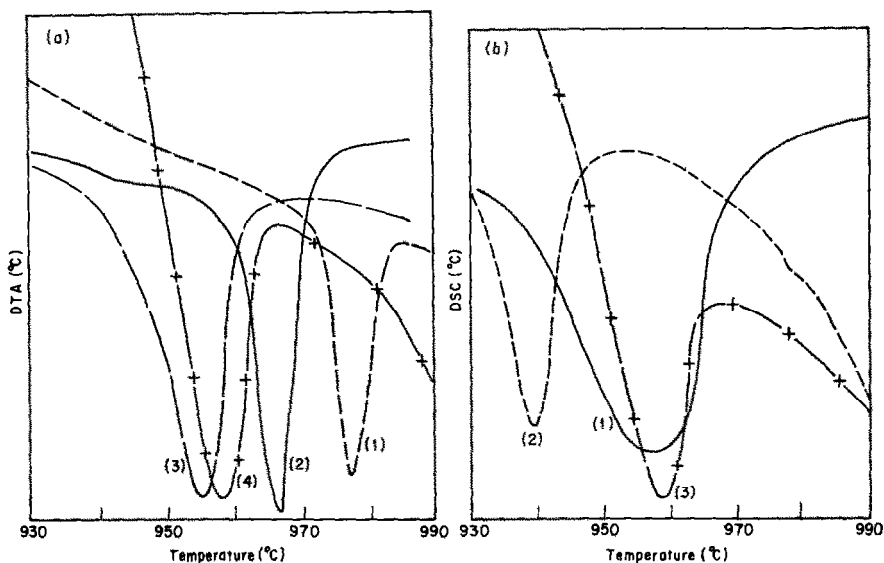


Fig. 6. (a) DTA curves for the formation of (curve 1) BaO via reaction (4); (curve 2)  $Y_2BaCuO_5$  via reaction (5); (curve 3)  $YBa_2Cu_3O_7$  via reaction (6); and (curve 4)  $YBa_2Cu_3O_7$  via reaction (1). Curve 4 is the same as the curve 1 in Fig. 1(a). These curves were scaled differently so that they had about the same heights in the figure. (b) DTA curves for the formation of (curve 1)  $BaCuO_2$  via reaction (7); (curve 2)  $YBa_2Cu_3O_7$  via reaction (8); and (curve 3)  $YBa_2Cu_3O_7$  via reaction (1). Curve 4 is the same as curve 1 in Fig. 1(a). These curves were scaled differently so that they had about the same heights in the figure.

The first mechanism considered is that  $BaCO_3$  self-decomposes, i.e.



and BaO reacts subsequently to form the 123 compound. Thermal analysis at  $1^\circ C \text{ min}^{-1}$  on pure  $BaCO_3$  powder bed showed that the self-decomposition of  $BaCO_3$  occurred between 970 and 985°C (curve 1 in Fig. 6(a)), and that the decomposition peak was completely isolated from the LT peak (curve 4 in Fig. 6(a)). These results indicate that the formation of the 123 compound was not initiated by the self-decomposition of  $BaCO_3$  as formulation in reaction (4). That is, if the 123 compound was formed following the reaction mechanism as suggested, the LT peak, which alone results in the complete formation of the 123 compound, would not have occurred at temperatures lower than 970°C.

Figure 7 shows part of the  $Y_2O_3$ -CuO-BaO phase diagram reported by Roth et al. [7]. The dotted line represents the compositions with fixed Y:Cu ratio of 1:3 and a Ba content less than that of the 123 compound. Firstly, it is noted that in the case of no decomposition of  $BaCO_3$ ,  $Y_2Cu_2O_5$  and CuO are the stable compounds. Consequently, reaction between  $Y_2O_3$  and CuO to form  $Y_2Cu_2O_5$  as described earlier is indeed thermodynamically feasible. Secondly, as more and more  $BaCO_3$  powder decomposes and

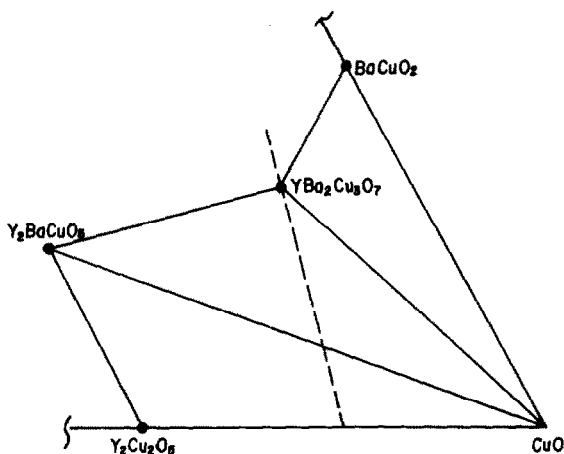
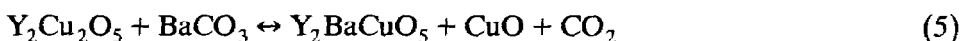


Fig. 7. Part of the phase diagram of  $Y_2O_3$ -BaO-CuO (according to Roth et al. [6]), with a Ba content less than that in  $YBa_2Cu_3O_7$ . The dotted line represents compositions of fixed Y:Cu = 1:3.

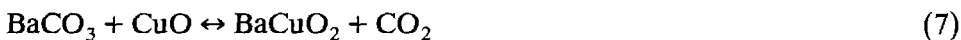
hence the 'effective' Ba content increases,  $Y_2BaCuO_5$  and the 123 compound could occur. Accordingly, the decomposition of  $BaCO_3$  in the present system could also follow the reactions



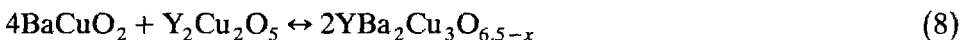
and



Furthermore, it was noted that in spite of the disagreements in their reported DTA characteristics, the earlier studies [4,5] all suggested the formation of  $BaCuO_2$  via



$BaCuO_2$  was indeed frequently reported [1–5] in the isothermal synthesis of the 123 compound, particularly at low temperatures ( $< 920^\circ C$ ). If reaction (7) does proceed in the present system, the 123 compound can be formed via



The DTA curves of reactions (5) and (6) peaked at 956 and 967°C, respectively (curves 2 and 3 in Fig. 6(a)), and both peaks were found, from XRD analysis, to result in the product compounds as formulated. Relative to the LT peak (curve 4), the peak of reaction (5) (curve 2) occurred at a higher temperature, while reaction (6) (curve 3) proceeded at a lower temperature. The fact is that reaction (6) cannot proceed unless reaction (5) takes place first to give  $Y_2BaCuO_5$ . Consequently, if reaction (5), along with reaction (6), contributes to the formation of the 123 compound within

the LT-peak region, it occurs only at temperatures where the reaction (5) peak and the LT peak overlap, i.e. within the tail region of the LT peak (curves 2 and 4 in Fig. 6(a)). This is consistent with the XRD results (Fig. 3(a)) which showed that the 211 compound did not occur until the later stage of the complete formation of the 123 compound.

The DTA curve of reaction (7), however, peaked (curve 1 in Fig. 6(b)) at the same temperature as the LT peak (curve 3), while the curve of reaction (8) occurred at  $\approx 940^\circ\text{C}$  (curve 2), about  $20^\circ\text{C}$  lower than the LT peak temperature. These results suggested that though self-decomposition of  $\text{BaCO}_3$  is not feasible at temperatures within the LT peak, formation of the 123 compound at these temperatures can be initiated by the formation of  $\text{BaCuO}_2$ , which can readily react to form the 123 compound via reaction (8). The absence of  $\text{BaCuO}_2$  in the XRD spectra acquired at  $1^\circ\text{C min}^{-1}$  may be because reaction (8), as evidenced by its lower peak temperature, proceeded much faster than reaction (7) at temperatures within the LT peak so that the amount of  $\text{BaCuO}_2$  formed in the powder was too small to be detected. Based on the DTA curves shown in Figs. 6(a) and 6(b) and on the XRD results, it is proposed that the formation of the 123 compound within the LT peak proceeds mainly via the reaction pathway consisting of reactions (7) and (8), and that the reaction pathway consisting of reactions (5) and (6) could take place in parallel but only within the tail region of the LT peak.

Although the reaction (5) peak (curve 2 in Fig. 6(a)) occurred at about the same temperature as the HT peak (Fig. 2), it is incorrect to assign the HT peak to the reaction pathway consisting of reactions (5) and (6) because, as mentioned earlier (Fig. 3(b)), the HT peak is associated with the destruction, rather than the formation, of the 123 compound. Rather, it is proposed that the occurrence of the HT peak is due to the melting of the already formed 123 compound. The 123 compound is known to melt incongruently and the melting temperature increases with oxygen partial pressure, ranging from  $\approx 970^\circ\text{C}$  in zero-oxygen atmosphere (e.g.  $\text{N}_2$ ) to  $\approx 1015^\circ\text{C}$  in air [8]. In this work the thermal analysis took place in air. However, as discussed earlier, during heating the powder bed will be filled with  $\text{CO}_2$  and the oxygen partial pressure will therefore be significantly reduced. It is noted that decomposition of  $\text{BaCO}_3$  can proceed at  $970^\circ\text{C}$  via reactions (4)–(6). Thus, it is possible that at heating rates higher than  $2^\circ\text{C min}^{-1}$  in this work,  $\text{BaCO}_3$  was not completely consumed within the LT peak range and that, as the temperature was increased to  $970^\circ\text{C}$ , the already formed 123 compound began to melt due to a low oxygen partial pressure. Incongruent melting of the 123 compound leads to solid  $\text{Y}_2\text{BaCuO}_5$  and a liquid Ba–Cu–O phase [8], from which  $\text{BaCuO}_2$  and CuO precipitate during cooling. This is consistent with the XRD results (Fig. 3(b)) which show continuous increase of  $\text{Y}_2\text{BaCuO}_5$  and  $\text{BaCuO}_2$  at temperatures above the HT peak. The HT peak did not occur at  $1^\circ\text{C min}^{-1}$

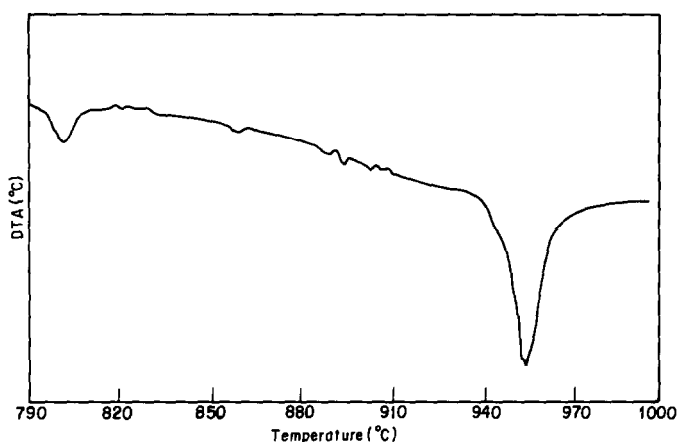


Fig. 8. DTA curve for the formation of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  at  $10^\circ\text{C min}^{-1}$ , using a sample size of 30 mg.

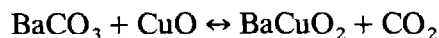
simply because all the  $\text{BaCO}_3$  had reacted to form the 123 compound before the temperature was raised to  $970^\circ\text{C}$ . In this case, at temperatures above the LT temperature, the oxygen partial pressure within the cell would be approximately equal to that in air and the already formed 123 compound would not melt until  $\approx 1015^\circ\text{C}$ .

Based on the above discussion, it is also clear that whether or not the HT peak will occur depends not only on the heating rate but also on the amount of reactant powder employed in the thermal analysis. That is, so long as the amount of the reactant powder is so small and the powder depth is so shallow that, as temperature is scanned beyond the LT peak, all the  $\text{BaCO}_3$  is completely consumed, the HT peak will never occur. Indeed, as shown in Fig. 8, when 30 mg, rather than 280 mg, of reactant powder was employed, only one LT peak was detected even at a heating rate as high as  $10^\circ\text{C min}^{-1}$ . This also explains, as mentioned in the Introduction, why different numbers of peaks were reported previously. For example, Jiang et al. [4] employed 30 mg of sample in their work and reported only one reaction peak, while Gadalla and Hugg [5] used 120 mg of samples and reported two peaks in the range of  $900\text{--}1000^\circ\text{C}$ .

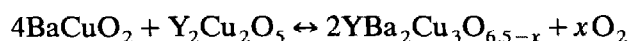
## CONCLUSION

The reaction mechanism taking place in the non-isothermal synthesis of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  from a mixture containing stoichiometric amounts of  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$  and  $\text{CuO}$  at constant heating rate was investigated using thermal analysis and X-ray diffraction analysis of linearly heated and subsequently quenched samples. It was found that  $\text{Y}_2\text{O}_3$  reacted extensively with  $\text{CuO}$  to form  $\text{Y}_2\text{Cu}_2\text{O}_5$  between  $820$  and  $920^\circ\text{C}$  prior to  $\text{YBa}_2\text{Cu}_3\text{O}_7$  formation,

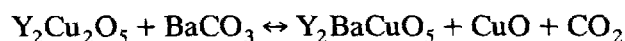
and that thermal analysis using  $Y_2Cu_2O_5$  as the Y source showed the same DTA peak at  $960^\circ C$  for  $YBa_2Cu_3O_7$  formation as when  $Y_2O_3$  is used. Thermal analysis of various possible 'sub-reactions' involving the decomposition of  $BaCO_3$  suggested that formation of  $YBa_2Cu_3O_7$  within this peak follows mainly the reaction pathway



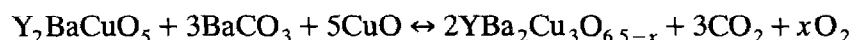
and



A second reaction pathway consisting of



and



also takes place but only at temperatures within the tail region of the peak.

Melting of  $YBa_2Cu_3O_7$ , which gave rise to an additional endothermic peak at  $970^\circ C$ , occurred for calcinations at high heating rates where  $BaCO_3$  was not completely consumed within the  $960^\circ C$  peak region. Controversies with regard to different numbers of DTA peaks reported in the earlier studies can be attributed to their different samples sizes, which determine if melting of  $YBa_2Cu_3O_7$  takes place.

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