Role of $Ba_2Cu_3O_5$ for the formation of $YBa_2Cu_4O_8$ in the presence of nitric acid

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The formation mechanism of $YBa_2Cu_4O_8$ in the presence of nitric acid was carefully studied by utilizing X-ray powder diffraction to monitor the reaction route. Contrary to the formation of $YBa_2Cu_3O_{7-\delta}$ in which $BaCuO_2$ was the dominant intermediate, an intermediate $Ba_2Cu_3O_5$ was identified and its yield was proportional to the amount of the nitric acid present in the formation of $YBa_2Cu_4O_8$. This seems to play an important role in determining the formation of the $YBa_2Cu_4O_8$ phase. To confirm the existence of this intermediate, $Ba_2Cu_3O_5$ was prepared from the same condition directly. Also, the structure similarity between $Ba_2Cu_3O_5$ and $BaCuO_2$ was discussed and emphasized.

1. Introduction

Since the discovery of the superconducting $La_{2-x}Ba_xCuO_4$ [1], the studies on ceramic cuprates superconductors have become extremely active due to the academic and technology interests. One of most studied ceramics is $YBa_2Cu_3O_{7-\delta}$ which has highest critical current density, J_c, in bulk materials. However, there are two other superconducting phases in the Y–Ba–Cu–O system, namely $YBa_2Cu_4O_8$ and $Y_2Ba_4Cu_7O_{14-x}$ [2, 3]. Both have superconducting transition temperatures, T_c, at 80 and 35 K, respectively. The former material also attracts a lot of attention due to its thermal and chemical stabilities. Moreover, the T_c temperature of $YBa_2Cu_4O_8$ could be enhanced upto 90 K as 10% Y component was replaced by Ca component [4]. Furthermore, thermal decomposition of the $YBa_2Cu_4O_8$ phase could lead to CuO and the $YBa_2Cu_3O_{7-\delta}$ with the J_c higher than 10^4 A cm^{-2} [5].

The preparation of the $YBa_2Cu_4O_8$ phase is tedious and difficult. In general, repeated grinding and long periods of heating such as several days were required to achieve high yield [6–9] unless the high oxygen pressure method was adopted [10–12]. Recently, we reported an excellent method to synthesize the $YBa_2Cu_4O_8$ phase in a short time through the help of nitric acid [13]. The details of formation mechanism of the above method are studied by monitoring the reaction processes so that the role of the nitric acid could be revealed.

2. Experimental procedure

A series of samples were prepared by mixing stoichiometric Y_2O_3 (Cerac), $Ba(NO_3)_2$ (Merck) and CuO (Alderich) and pouring into beakers in which five nitric solutions with different concentration were present. The whole volume of the nitric acid solution was fixed to 100 ml while the volume of the nitric acid increased from 0, 25, 50, 75 to 100 ml. Dark grey and green-blue residues were obtained after stirring and heating to dry. The residues were first calcined at
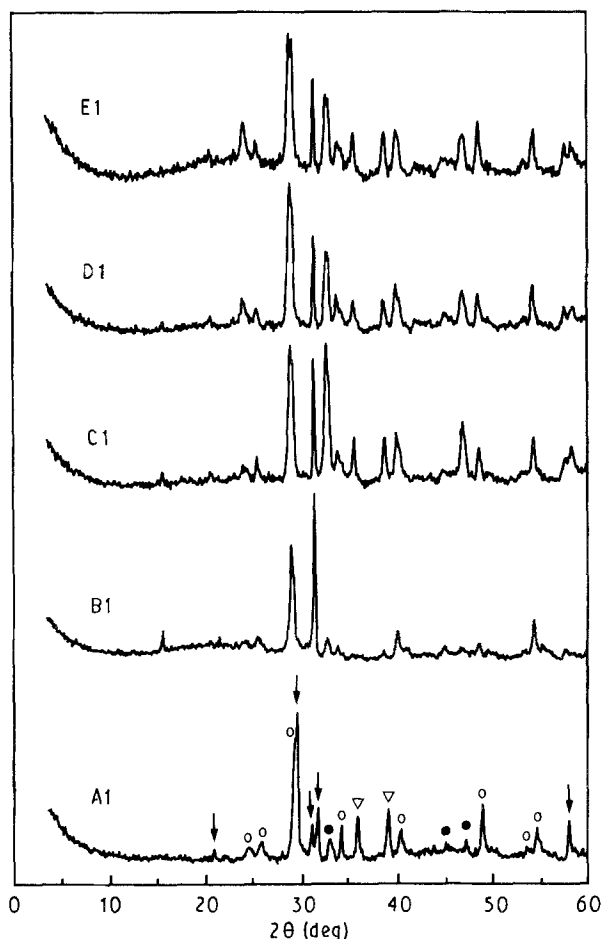

Figure 1 XRD patterns for the samples calcined at 750 °C for 8 h with different amounts of nitric acid added: (●) $YBa_2Cu_4O_8$; (○) $Ba_2Cu_3O_5$; (▽) CuO and (↓) unknown phases.

750 °C for 8 h in an oxygen atmosphere, then followed by sintering at 805 °C for three different periods of time (15, 33 and 48 h, respectively). To confirm the existence of $Ba_2Cu_3O_5$, it was also prepared by a similar way as the above treatments. X-ray powder diffraction patterns were taken for the calcined and sintered products to study the formation mechanism by employing a powder diffractometer (SHIMAZU XRD3A) with CuK_α radiation. A standard four probe resistance measurement was conducted to confirm the electrical property while a d.c. magnetometer (SQUID Quantum Design) was utilized to characterize the magnetic properties of the products.

3. Results and discussion

For easy comparisons, the reactions with different amounts of nitric acid added were abbreviated as A, B, C, D, and E, respectively, while arabic numbers 1–4 represented different heat treatment steps. The X-ray powder patterns for the products through same heat treatment but with the different concentration of nitric acid used are shown in Figs 1–4. In Fig. 1, the products, which have been calcined at 750 °C for 12 h, contained the following components: $YBa_2Cu_4O_8$, $Ba_2Cu_3O_5$, CuO and unknown phases. It is noted that the amount of $Ba_2Cu_3O_5$ was proportional to amount

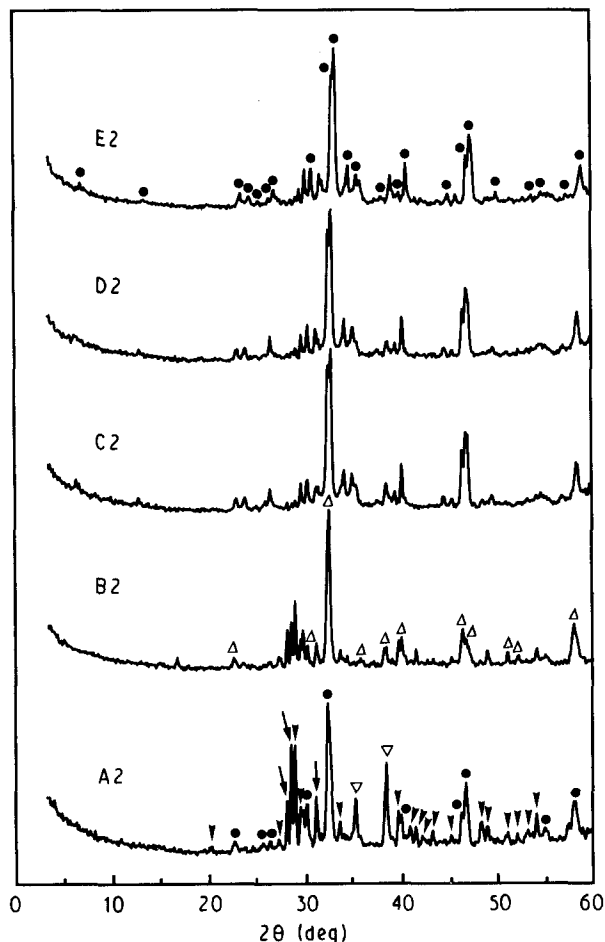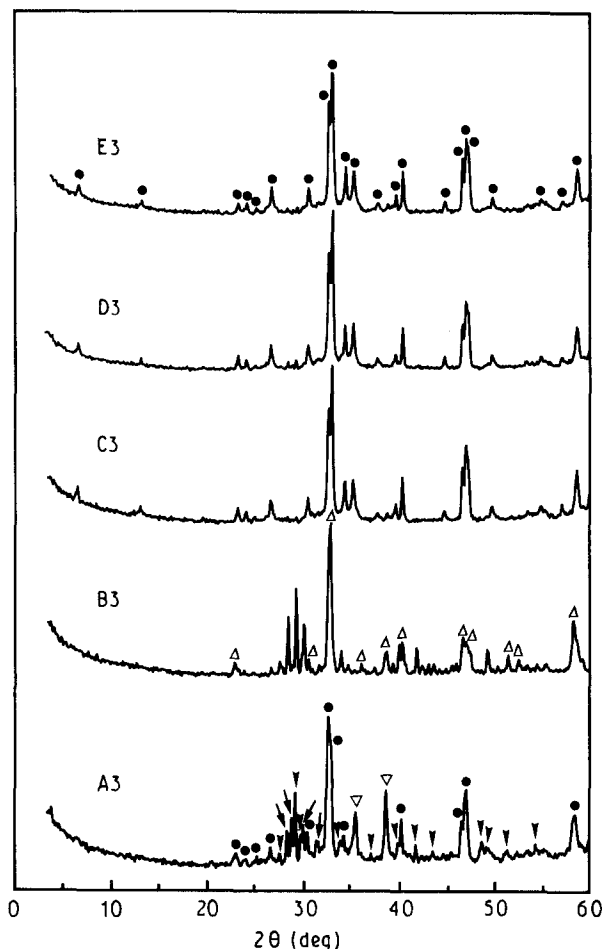*Figure 3* XRD patterns for the samples sintered at 805 °C for 33 h with different amounts of nitric acid added: (●) $YBa_2Cu_4O_8$; (○) $Ba_2Cu_3O_5$; (▽) CuO; (▼) $BaCuO_2$; (△) $YBa_2Cu_3O_{7-\delta}$ and (↓) unknown phases.

of nitric acid added and only a negligible amount of $YBa_2Cu_4O_8$ was present in reaction A1. In Fig. 2, the appearance of $YBa_2Cu_4O_8$ became significant for reactions C2, D2 and E2 while only $YBa_2Cu_3O_{7-\delta}$ and CuO were observed in reaction B2. The strong reflection peaks of CuO in A2 suggested that $YBa_2Cu_3O_{7-\delta}$ coexisted in A2. After sintering at 805 °C for 33 h, the yield of $YBa_2Cu_4O_8$ became dominant in reactions C3, D3 and E3 while no 1 2 4 phase was found in reaction B3 as shown in Fig. 3. As the sintering time prolonged to 44 h, nearly all single phase $YBa_2Cu_4O_8$ was obtained in reactions C4–E4, still no $YBa_2Cu_4O_8$ could be detected for B4 in Fig. 4. From the above results, it is clearly indicated that the $YBa_2Cu_4O_8$ phase could be successfully synthesized with the amount of nitric acid greater than 50 ml and the sintering time longer than 33 h. For the reactions with 25 ml nitric acid present, the as-sintered products were $YBa_2Cu_3O_{7-\delta}$ and CuO.

It is speculated that the intermediate $Ba_2Cu_3O_5$ seemed to play a determining role for the formation of $YBa_2Cu_4O_8$ phase. Therefore, a pure phase of $Ba_2Cu_3O_5$ was prepared by the same way as the above reactions. The as-prepared $Ba_2Cu_3O_5$, which was calcined at 750 °C for 12 h under an oxygen atmosphere, was confirmed to be a mixture of low and high temperature form of $Ba_2Cu_3O_{5+\delta}$ by the X-ray

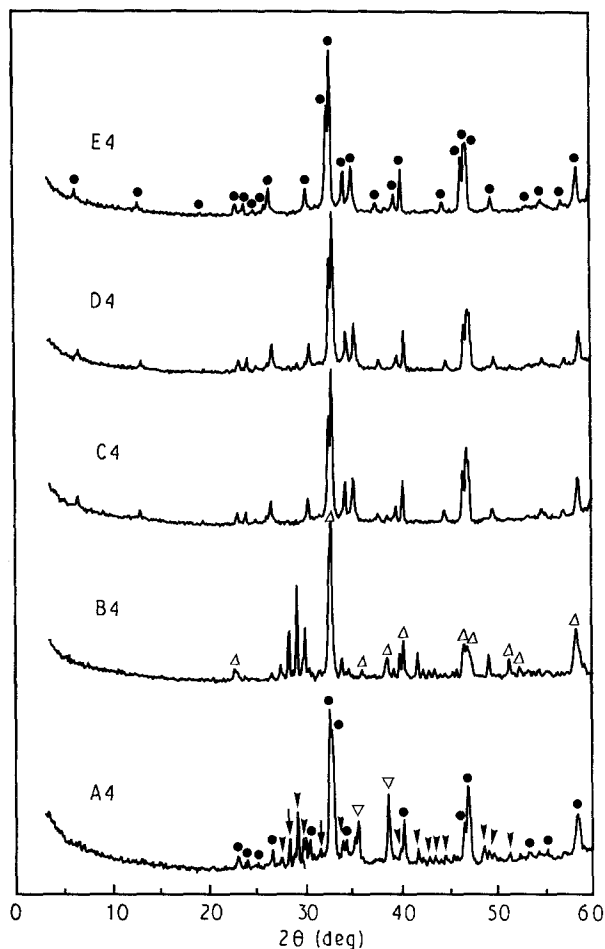*Figure 2* XRD patterns for the samples sintered at 805 °C for 15 h with different amounts of nitric acid added: (●) $YBa_2Cu_4O_8$; (○) $Ba_2Cu_3O_5$; (▽) CuO; (▼) $BaCuO_2$; (△) $YBa_2Cu_3O_{7-\delta}$ and (↓) unknown phases.

Figure 4 XRD patterns for the samples sintered at 805 °C for 48 h with different amounts of nitric acid added: (●) $YBa_2Cu_4O_8$; (○) $Ba_2Cu_3O_5$; (∇) CuO; (▼) $BaCuO_2$; (△) $YBa_2Cu_3O_{7-\delta}$ and (↓) unknown phases.
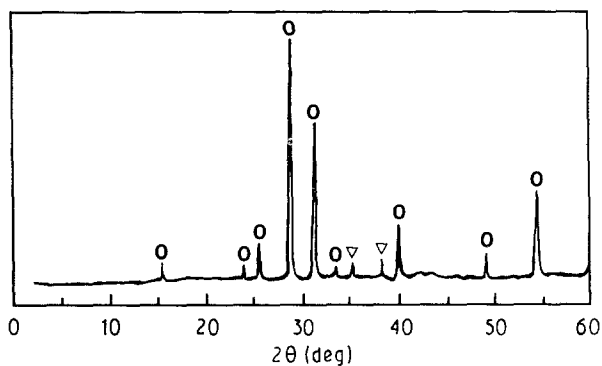
Figure 5 XRD pattern for as-prepared $Ba_2Cu_3O_5$: (○) $Ba_2Cu_3O_5$ and (∇) CuO.

powder pattern shown in Fig. 5. It has been reported that $BaCuO_2$ was a dominant intermediate during the preparation of the Y-1 2 3 phase [14–16]. Therefore, the differences between intermediate $Ba_2Cu_3O_5$ and $BaCuO_2$ seemed to determine whether to form the desired $YBa_2Cu_4O_8$ or $YBa_2Cu_3O_{7-\delta}$ phase. In other words, the appearance of $Ba_2Cu_3O_5$ favoured the formation of $YBa_2Cu_4O_8$ while the existence of $BaCuO_2$ would favour producing $YBa_2Cu_3O_{7-\delta}$. The structure relationship between $Ba_2Cu_3O_5$ and $BaCuO_2$ has been discussed [17]. Basically, they are

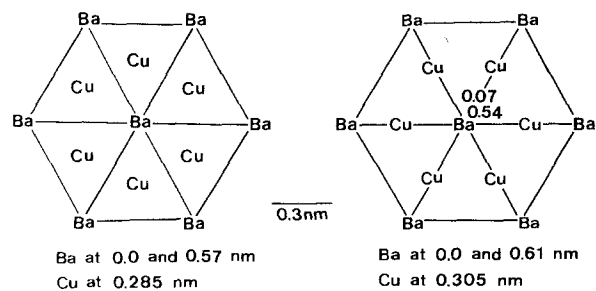*Figure 6* Arrangements of Ba and Cu atoms for idealized $Ba_2Cu_3O_5$ (left) and a related structural unit from $BaCuO_2$ (right). Heights (nm) for Ba atoms as centre of $BaCuO_2$ structural unit (right) are indicated.

very similar in metal atoms arrangement especially for Ba atoms. Fig. 6 was reproduced from [17] to demonstrate this relationship . Clearly, the major difference is the relative positions of Cu atoms if the oxygen atoms were ignored. Also, the distances between Ba and Ba or Ba and Cu atoms in $BaCuO_2$ are longer than those in $Ba_2Cu_3O_5$. It has been suggested that the $Ba_2Cu_3O_5$ was derived from the $2BaCuO_2 + CuO$ through the diffusion reaction [17]. This seemed to be less favourable because $Ba_2Cu_3O_5$ was more stable at lower temperature while $BaCuO_2$ could be stable upto 900 °C. Moreover, an incommensurate structure and nonstoichiometry of oxygen atoms was observed in $Ba_2Cu_3O_5$ [17]. Thus, the reactivity or structure characteristic of $Ba_2Cu_3O_5$ might be the main cause for the formation of $YBa_2Cu_4O_8$ phase.

To confirm the phase purity of the as-prepared $YBa_2Cu_4O_8$ phase, electrical and magnetic properties of products were characterized by the standard four probe resistance technique and SQUID magnetometer. The results with T_c at 80 K are depicted in Figs 7 and 8, respectively, and are in good agreement with the literature results.

4. Conclusion

The intermediate $Ba_2Cu_3O_5$ has been prepared and confirmed to play a dominant role in the formation of $YBa_2Cu_4O_8$ phase as the nitric acid was added. The close structural relationship between $Ba_2Cu_3O_5$ and $BaCuO_2$ was explored to rationalize the difference in
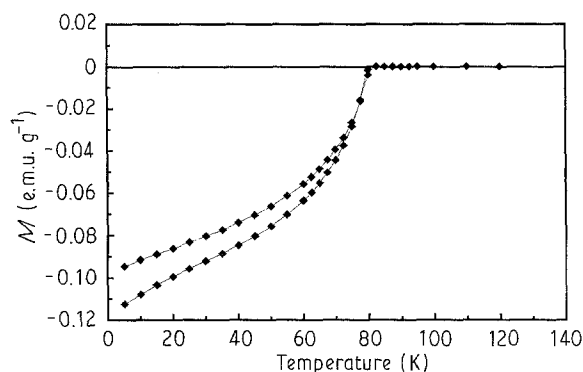

Figure 7 Field cooling magnetization data for as prepared $YBa_2Cu_4O_8$ sample measured in a field of 1.6×10^3 Am^{-1} between 5 and 120 K.
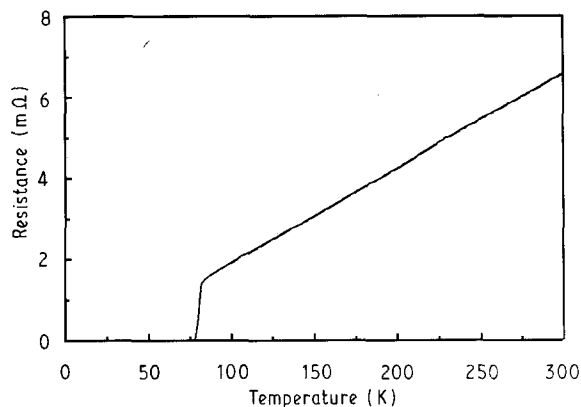
Figure 8 Temperature dependence resistance for as prepared $YBa_2Cu_4O_8$ sample.

their reactivity. In general, the appearance of $Ba_2Cu_3O_5$ favoured the formation of $YBa_2Cu_4O_8$ phase while the presence of $BaCuO_2$ favoured forming $YBa_2Cu_3O_{7-\delta}$.

Acknowledgements

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