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AN INVESTIGATION INTO THE SELF-PROPAGATING HIGH TEMPERATURE SYNTHESIS (SHS) OF SUPERCONDUCTING CERAMICS BY THERMAL METHODS

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The SHS route is based on the well-known thermite reaction, in which a strongly exothermic reaction can sustain itself and propagate in the form of a combustion wave until the reactants have been completely consumed. The successful application of the method to the synthesis of superconducting ceramics of stoichiometry $RBa_2Cu_3O_y$ (R = Y, Er, Yb) is reported. The 123 phase was obtained when pellets of R_2O_3, BaO_2 and Cu metal in the correct proportions were dropped into a heater held at 800°C in an oxygen atmosphere and left there for only 10 minutes. Thermal methods (DSC and DTA) are excellent techniques with which to investigate the dependence of the reaction on heating rate, atmosphere and starting composition.

Keywords: self-propagating high temperature synthesis (SHS), superconducting ceramics

Introduction

Self-propagating high-temperature synthesis (SHS), developed by Merzhanov and Borovinskaya [1], has become an important route for the fabrication of refractory materials by igniting compacts of reactive powders [2]. Two major advantages of the method are the elimination of the need for high temperature furnaces, thus greatly reducing energy consumption, and the formation of high-purity products, since the high temperature generated during the synthesis drives off most of the volatile contaminants present.

The discovery of 'high-temperature' superconducting ceramics is now well-known. The most thoroughly investigated of these systems is that based on $YBa_2Cu_3O_y$ or YBCO, first reported by Wu *et al.* [3] in 1987. Since then numerous papers have been published concerned with this and related phases, but their processing normally requires two stages, which take an inconveniently long period of time. We have demonstrated [4] that the use of the SHS process can sig-

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nificantly reduce the time and energy required to synthesise these superconducting ceramics. The aim of this paper is to show that the application of differential scanning calorimetry (DSC) and differential thermal analysis (DTA) provides useful data relating to the dependence of the SHS process on heating rate, atmosphere and initial composition.

Experimental

The SHS procedure and the chemicals used have been described elsewhere [4]. DSC (on samples of about 10 mg) and DTA (about 30 mg) curves were obtained using a DuPont 2000 TA, in controlled atmospheres of either nitrogen or oxygen (15 ml/min flow rate).

Results and discussion

The exothermic nature of the reaction between Y_2O_3, BaO_2 and Cu metal in molar proportions of 0.5:2:3 on heating in oxygen is clearly illustrated by the DSC curves shown in Fig. 1. As the heating rate was increased from 10 deg/min to 50 deg/min, the main exothermic peak became more intense, increasing in magnitude (as indicated by the area under the peak) and in peak temperature which increased from 277° to 309°C. To investigate reactions that occur above 600°C, the same composition was heated in the DTA apparatus up to 1100°C at

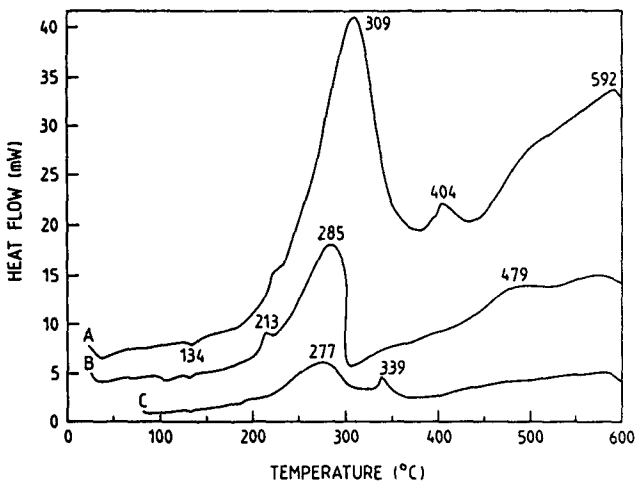

Fig. 1 DSC curves for samples of Y_2O_3, BaO_2 and Cu (0.5:2:3; 12 mg) heated in oxygen at (A) 50 deg/min, (B) 20 deg/min and (C) 10 deg/min

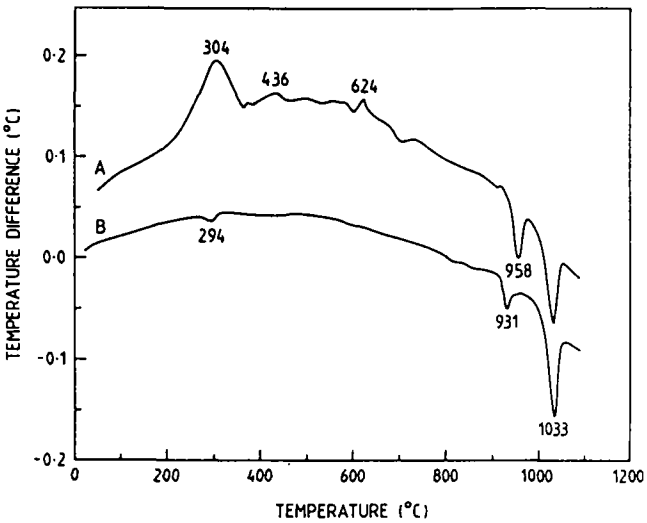

Fig. 2 DTA curves for samples of Y_2O_3, BaO_2 and Cu (0.5:2:3; 28 mg) heated in oxygen at 20 deg/min (A) reaction mixture, (B) after SHS

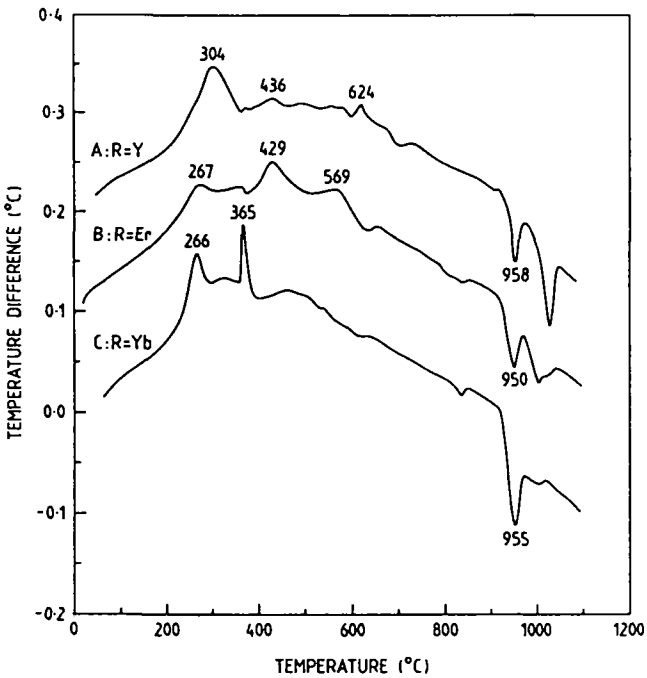

Fig. 3 DTA curves for samples of R_2O_3, BaO_2 and Cu (0.5:2:3) heated in oxygen at 20 deg/min (A) R = Y, (B) R = Er, (C) R = Yb

20 deg/min in oxygen (Fig. 2, curve *A*). The low-temperature part of the DTA curve is essentially similar to the DSC curve obtained at the same heating rate, but also indicates further reactions and melting phenomena, notably at 958° and 1033°C. A sample that had undergone the SHS process described above gave the DTA curve shown in Fig. 2*B*, which again indicates the high-temperature endotherms, but not the exotherms in the range 200°–700°C. The exothermic reactions observed by DSC and DTA in this temperature range must, therefore, be associated with the reactions that take place during the SHS process, whereas the endothermic events occurring above 900°C are attributed to melting of the reaction products formed during either SHS or the heating in the thermal analysis equipment.

When yttrium oxide was replaced by either erbium oxide or ytterbium oxide, the DTA curves were closely similar to those shown in Fig. 2, although the peak temperatures were slightly different. DTA curves obtained using all three lanthanide oxides are compared in Fig. 3 and the similarity of the curves indicates that equivalent reactions occurred at approximately the same temperatures. DTA curves of Er_2O_3- and Yb_2O_3-containing mixtures after SHS were closely similar to that shown in Fig. 2B, with small endotherms at 295°C and larger endotherms

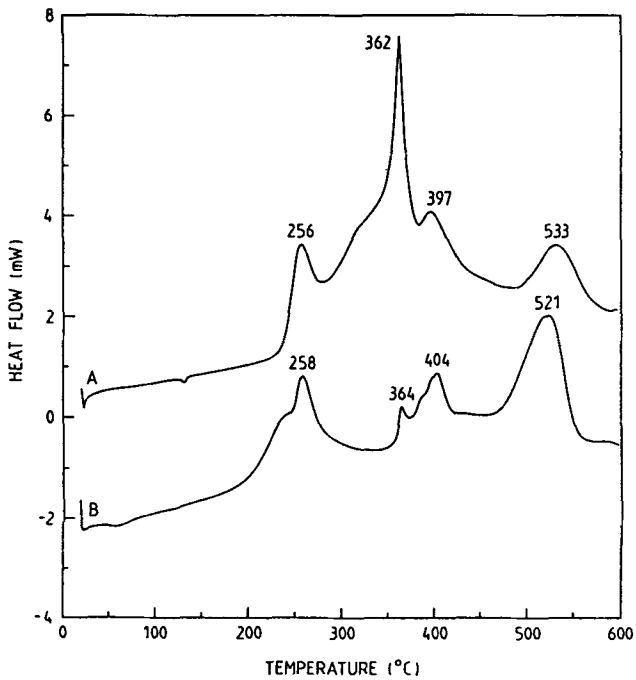

Fig. 4 DSC curves for samples of R_2O_3, BaO_2 and Cu (0.5:2:3) heated in nitrogen at 10 deg/min (A) R = Y, (B) R = Er

at 931°, 940° and 956°C and at 1033°, 1012° and 1024°C for the Y, Er and Yb systems, respectively.

When mixtures of the same molar proportions were heated in nitrogen instead of in oxygen, exothermic reactions were again observed using DSC. The curves for Y- and Er-containing systems are shown in Fig. 4 and can be seen to be similar. Although the magnitude of the peaks varies with the metal oxide used, the temperatures are remarkably consistent (256° cf. 258°C, 362°cf. 364°C, 397° cf. 404°C, and 533°cf. 521°C for Y- and Er-containing systems, respectively).

To understand the reaction mechanism and to attribute the peaks observed in the DSC and DTA curves described above, binary mixtures were prepared as follows: (*A*) $0.5Y_2O_3 + 2BaO_2$, (*B*) $2BaO_2 + 3Cu$, and (*C*) $0.5Y_2O_3 + 3Cu$, i.e. retaining the same relative proportions as required in the ternary system to form $YBa_2Cu_3O_y$. DSC curves obtained on heating these mixtures in nitrogen at 10 deg/min are shown in Fig. 5. It is immediately apparent that there is no reaction in system (*C*) and therefore that the reactions observed in the ternay system are due to systems (*A*) and (*B*) and their reaction products. X-ray diffraction studies reported elsewhere [4] indicate that yttrium oxide and barium peroxide react together readily to form Y_2BaO_4. The vigorous reaction, even in a nitrogen atmosphere, between copper metal and barium peroxide to form $BaCuO_2$ is clearly indicated by the strong exotherm at 531°C in Fig. 5, curve *B*. The combination of the DSC curves of (*A*) and (*B*) is similar to those shown for the ternary systems in Fig. 4. Evidence from X-ray diffraction studies of fired samples has established that after the initial formation of Y_2BaO_4 and $BaCuO_2$, the phases $YBa_2Cu_3O_y$ and Y_2BaCuO_5 are subsequently formed [4]. No Y– Cu binary phase, such as $Y_2Cu_2O_5$, was observed as a reaction intermediate.

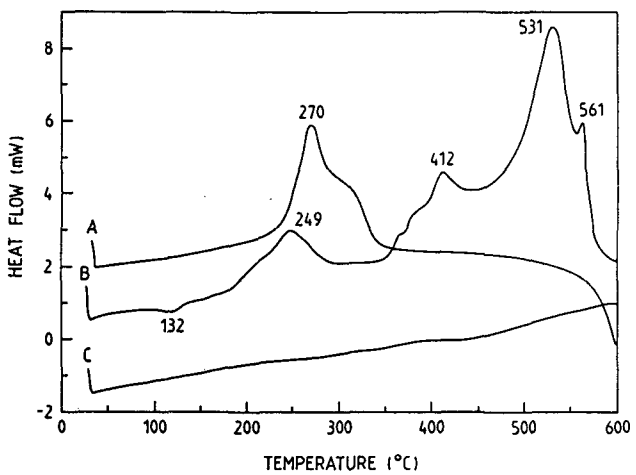

Fig. 5 DSC curves of (A) $0.5Y_2O_3 + 2BaO_2$, (B) $2BaO_2 + 3Cu$, and (C) $0.5Y_2O_3 + 3Cu$, heated in nitrogen at 10 deg/min

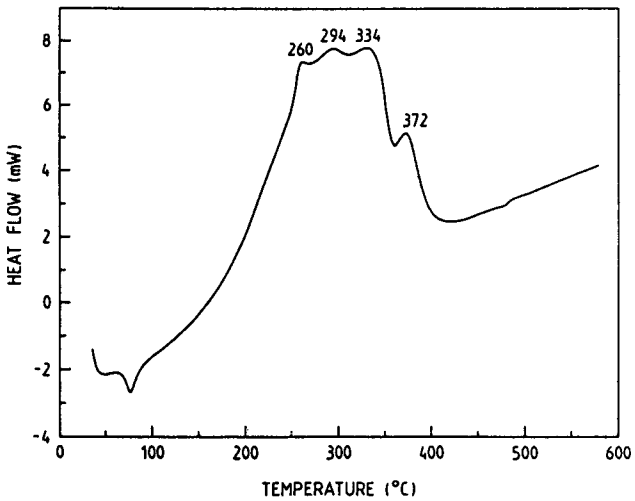

Fig. 6 DSC curve of Y_2O_3 and BaO_2 (0.5:2) heated in oxygen at 50 deg/min

The even more vigorous nature of these reactions in an oxygen atmosphere is strikingly demonstrated by the DSC curves shown in Figs 6 and 7. Note that the scale on the y-axis in Fig. 7 is much different from that used in Figs 5 and 6, indicating that the presence of oxygen has had a marked effect on the reaction in the system incorporating copper metal. The importance of the redox reaction involving copper metal is also demonstrated by the DSC curves shown in Fig. 8, which were all obtained on heating in oxygen at 50 deg/min. The most vigorous reaction was observed in the system containing copper metal, followed by that containing

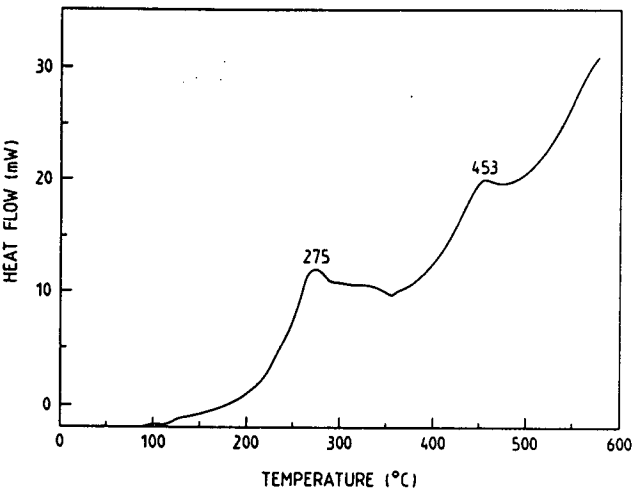

Fig. 7 DSC curve of BaO_2 and Cu (2:3) heated in oxygen at 50 deg/min

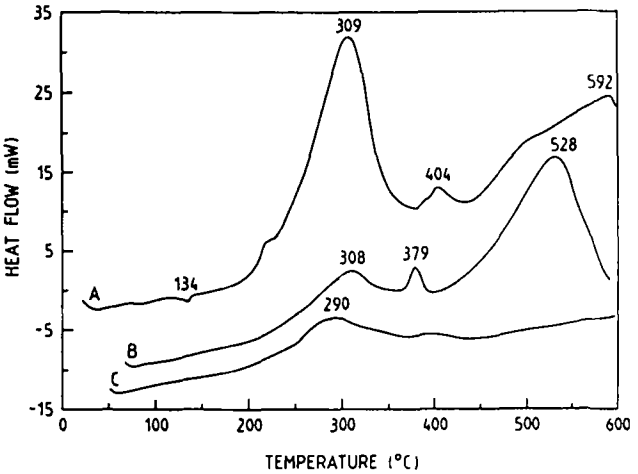

Fig. 8 DSC curves for samples heated in oxygen at 50 deg/min (A) Y_2O_3, BaO_2 and Cu (0.5:2:3), (B) Y_2O_3, BaO_2, and Cu_2O (0.5:2:1.5), (C) Y_2O_3, BaO_2 and CuO (0.5:2:3)

copper(I) oxide and finally copper(II) oxide. XRD examination of reaction products from SHS processes carried out at various temperatures showed that BaO_2 disappeared by 300°C when copper metal was present, but not until 600°C when either Cu_2O or CuO was present in the reaction mixture. Similarly it was established [4] that BaO_2 is more reactive in the SHS process than $BaCO_3$. It is concluded that to obtain an effective SHS reaction, barium peroxide acts as a strong oxygen donor and copper metal as an oxygen acceptor. Cu_2O gives a better reaction than CuO because it can still act as a reducing agent.

Conclusions

The SHS method for making dense ceramics can be extended to include the new family of superconductors based on $RBa_2Cu_3O_y$, where R = Y, Er or Yb. The best results were obtained in systems incorporating copper metal and barium peroxide rather than those incorporating either of the copper oxides or barium carbonate. The magnitude of the exothermic reactions associated with the SHS process is readily investigated using DSC, although this technique is limited to relatively low temperatures. DTA can be used to extend the range of temperatures investigated and to show the melting of the reaction products above 900°C. To simulate most closely the conditions pertaining during the SHS process, we recommend the use of very high heating rates, such as 50 deg/min.

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References

1 G. Merzhanov and I. P. Borovinskaya, Dokl. Akad. Nauk. SSSR, Chem. Sect., 204 (1972) 429.
2 R. W. Rice, J. Materials Sci., 26 (1991) 6533.
3 M. K. Wu *et al.*, Phys. Rev. Lett., 58 (1987) 908.
4 H. J. Chen and J. H. Sharp, J. Materials Sci. Letters, 11 (1992) 1223.

Zusammenfassung — Der Weg der SHS basiert auf der wohlbekannten Thermitreaktion, in der sich eine stark exotherme Reaktion selbst aufrechterhalten und in Form einer Verbrennungswelle ausbreiten kann, bis alle Reaktanden vollständig verbraucht wurden. Es wird die erfolgreiche Anwendung dieser Methode bei der Herstellung von supraleitender Keramik der Zusammensetzung $RBa_2Cu_3O_y$ (R=Y, Er, Yb) beschrieben. Die 123 Phase erhält man, wenn Pellets aus R_2O_3, BaO_2 und metallischem Cu im richtigen Verhältnis in einen auf 800°C thermostierten Erhitzer mit Sauerstoffatmosphäre geworfen und dort nur 10 Minuten lang belassen werden. Thermische Methoden (DSC und DTA) sind ausgezeichnete Methoden, um die Abhängigkeit der Reaktion von Aufheizgeschwindigkeit, Atmosphäre und Ausgangszusammensetzung zu untersuchen.