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THERMAL ANALYSIS AND THE PROCESSING OF ELECTRONIC AND MAGNETIC CERAMICS

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Abstract

Control of processing parameters, in both conventional ceramic routes and novel gel processing routes, is vital in the production of electronic and magnetic ceramics. The role of thermal analysis in the provision of basic data for the understanding of both types of processing route is discussed with special emphasis being placed upon the production of 1–2–3 YBCO superconductors and MgO-based soft ferrite materials for TV deflection unit applications.

Keywords: dilatometry, DSC, DTA, EGA, electronic ceramics, magnetic ceramics, superconductors, TG

Introduction

As electronic and magnetic ceramics assume greater and greater importance in today's technology, control of their production and processing becomes ever more important. In particular this is so because many of the commonly used materials, such as ferrites for chokes, potentiometer cores and deflection yokes in TV focusing systems, are extremely complex mixtures of oxides. For example, a soft ferrite for a TV yoke ring may typically be composed of a mixture of MgO, ZnO, MnO and Fe_2O_3 plus various sinter aids which require to be reacted to produce a chemically homogeneous spinel oxide phase. It is clear that the potential reactions on heating of such mixtures need to be fully understood so that calcination treatments may be optimised. Thermoanalytical techniques are the ideal methods for assessing such reaction possibilities. Similarly, in the recent, rapidly growing area of activity in high T_c superconductors knowledge of decomposition/reaction processes is required to optimise processing conditions so that the best superconducting properties of the materials may be realised. For yttrium-barium-copper oxide high T_c superconductors ($Y_1Ba_2Cu_3O_{7-x}$, YBCO 123) processed by conventional ceramic technology, thermal decomposition and reactions between $BaCO_3$, Y_2O_3 and CuO form the basis of the production method. Similar situations exist for the other high T_c superconductors based on the Bismuth-

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strontium-calcium-copper oxide (BSCCO) and thallium-barium-calcium-copper oxide (TBCCO) systems. Examples taken from soft magnetic ferrites and 123 YBCO superconductors will be used to illustrate the application of thermoanalytical techniques in the study of conventional ceramic processing methods.

There has been a tremendous interest shown in recent years in novel chemical processing routes for the production of ceramic materials. All the new techniques have the aims of increasing chemical homogeneity and purity, relative to that achieved conventionally, whilst, at the same time, exerting potential control of particle size and morphology. Many process routes are designed to transfer the chemical homogeneity, that may be achieved in a well stirred aqueous solution, into the solid state, usually via the production of a precursor. This precursor may, for example, be a gel, a co-precipitated mixture of salts or a freeze-dried mixture of salts.

As an example of one of these newer process routes, and the application of thermoanalytical techniques to the study of the process route, the use of citrate gel processing, in which citric acid is used to gel nitrate salt solutions will be considered. To be consistent with the examples taken for illustration of the use of thermoanalytical techniques in the study of conventional ceramic processing, soft magnetic ferrites and YBCO 1–2–3 based superconductors will be discussed.

Examples of other electronic and magnetic ceramics could have been included in the present paper. However, lead zirconate titanate (PZT), as an example of a piezoelectric ceramic, and BSCCO thin films, as another example of a superconducting ceramic are included elsewhere in this volume.

Conventional ceramic processing

Conventional ceramic processing is a basic multistage process. Raw materials, which may be oxides, carbonates, hydroxides or mixtures of these, are mixed in an attempt to obtain maximum chemical homogeneity. This mixing is usually carried out in rod or ball mills of some kind. Following the mixing operation a calcination of the mixture is carried out to allow decomposition and some degree of reaction of the oxides or other compounds to produce the required product. Depending upon the ceramic up to 100% complete reaction may be required after calcination, although a value of 75% reaction is typically achieved. During calcination and reaction, sintering and agglomeration of the ceramic particles occurs and so a following milling stage is needed to break down the agglomerates to give a powder with correct flow properties and pressability. Often the milled powders may be taken into a slurry and spray dried to yield controlled spherical agglomerates which have good die-filling and pressing properties.

Once the ceramic powder has been obtained of the correct quality it is formed or shaped by a range of methods, which includes simple uniaxial pressing. CIPping and HIPping or plastic extrusion. After the correct shape has been obtained the ceramic is sintered to obtain a dense, solid product having the required properties.

It is clear that thermal analysis may be used to gain much vital and basic knowledge which is required for the control of the conventional processing scheme. In particular TG, DTA, DSC and dilatometry may be used to study the calcination and sintering parts of the process. EGA may also give useful data for the understanding of calcination reactions.

Production of soft ferrites

As indicated previously a soft ferrite for use as a deflection yoke ring for a T.V. receiver or VDU may be comprised of MgO, ZnO and Fe_2O_3 with some MnO and other sinter aids, which have ideally been reacted to produce a chemically homogeneous magnetic ferrite having a spinel structure. Standard TG and DTA may be used to study the reactions which give the spinel phase as both mass change and enthalpic effects are associated with the reactions. However, dilatometry is often a more effective technique to follow the reactions because there is a substantial volume expansion associated with the production of the spinel phase from the individual oxides [1]. An added advantage of the use of dilatometry is that the temperature required for sintering and densification of the ferrite may also be determined.

Figure 1 shows dilatometric curves obtained at a heating rate of 200 $deg \cdot h^{-1}$ in air for compacts of ZnO and Fe_2O_3 and MgO and Fe_2O_3. The expansions associated with the formation of the spinel phases $ZnFe_2O_4$ and $MgFe_2O_4$ are clearly evident. It is also apparent that $ZnFe_2O_4$ forms at a lower temperature than $MgFe_2O_4$. This difference in reactivity is evident in complex mixtures in that $ZnFe_2O_4$ is always the first spinel phase to be detected by XRD of partially-reacted mixtures. As a result it is clear that the reaction sequence for the formation of the spinel phase in a complex mixture is one in which $ZnFe_2O_4$ forms first and sequentially reacts with other oxides to yield the complex ferrite.

Figure 1 also shows that the beginning of densification of the powder compacts, i.e. the onset of sintering, occurs at a temperature of 900°C in the $ZnO-Fe_2O_3$ system and a temperature of approximately 1000°C in the $MgO-Fe_2O_3$ system. This behaviour again reflects the difference in reactivity in the systems.

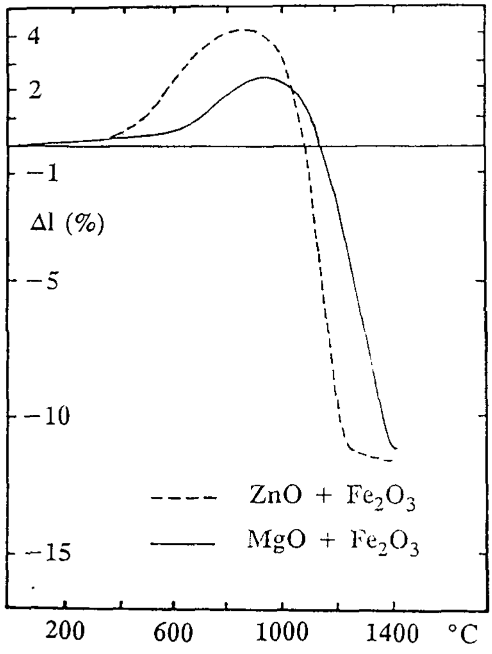

Fig. 1 Dilatometric data for reaction of ZnO with Fe_2O_3 and MgO with Fe_2O_3 to give the respective spinel phases. (Atmosphere air, flow rate 300 ml·min^{-1}; heating rate 200 deg·h^{-1})

The degree of reaction in a calcined batch of ferrite powder may be assessed using dilatometry. Figure 1 showed data only for the formation of $ZnFe_2O_4$ and $MgFe_2O_4$ from their individual oxides. Figure 2 shows a comparison of dilatometric data obtained for a complex ZnO, MgO, MnO, Fe_2O_3 mixture in the un-reacted state and in the pre-fired (calcined) state. The difference in the curves on heating to approximately 1050°C is a direct result of absence of the spinel phase in the raw mixture and the presence of 100% spinel in the pre-fired sample. Consequently, the degree of reaction of any partially-reacted mixture may be assessed by comparison with a 'calibrated' set of dilatometric data for reaction in the system under study.

Soft ferrites for deflector ring applications are frequently made from manganese zinc ferrite (without any MgO content) to give improved magnetic properties. In the conventional manufacture of these ferrites added difficulties, associated with both mechanical properties and magnetic properties, are encountered because of oxidation during cooling from the sintering temperature (typically 1340°C), unless there is control of the oxygen potential of the gas phase [2]. This relationship between processing conditions, oxygen stoichiometry, magnetic properties and mechanical strength in MnZn ferrites has been a subject of much study [3–5]. TG and dilatometry have proved particularly useful in such studies because any post-sintering oxidation, which causes free Fe_2O_3 to be formed, is associated with both a mass gain and a significant dimensional change.

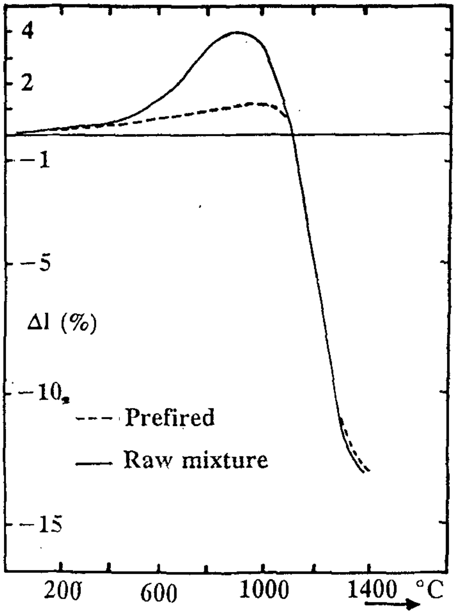

Fig. 2 Dilatometric data for raw mixture and pre-fired mixture for MgO-based ferrite. (Atmosphere air, flow rate 300 ml·min^{-1}; heating rate 200 deg·h^{-1})

Production of Y–Ba–Cu–O superconductor

As indicated earlier the most frequently used method for the production of bulk YBCO superconductor is a conventional ceramic route in which Y_2O_3, $BaCO_3$ and CuO are mixed, calcined, milled, pressed and sintered. An added complication in the processing of this ceramic is concerned with the oxygen content. For good superconducting properties the oxygen content in the formula $YBa_2Cu_3O_{7-\delta}$ of the so-called 123 phase should be as close to O_7 as possible. However, at the temperature needed for full decomposition of the carbonate and for the sintering of particulate material (≅950°C), the equilibrium oxygen content in an oxygen atmosphere at a pressure of 1 bar give δ approximately equal to 0.7 [6, 7]. The lowering in oxygen content results in the well known orthorhombic (superconducting) phase to tetragonal (semiconducting) phase transition.

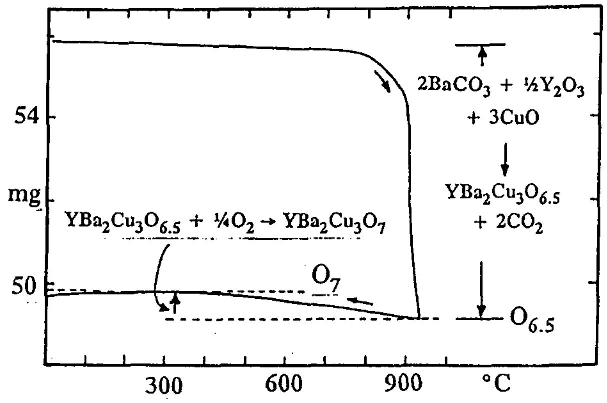

Fig. 3 TG study of the preparation of YBCO from $BaCO_3$, Y_2O_3 and CuO. (Atmosphere, oxygen; heating/cooling rate 10 deg·min^{-1}) (After Irvine *et al.* [8])

TG has been used successfully [8, 9] to demonstrate the reaction to form the YBCO superconductor and the re-oxygenation of the reacted superconductor. Figure 3 shows data determined by Irvine *et al.* [8] for these reactions. Reaction begins at 750°C, with a consequent mass loss until approximately 940°C when the product $YBa_2Cu_3O_{6.5}$ has been obtained. On controlled cooling at a rate of 10 deg·min^{-1}, oxygen uptake, which gives the increase in mass seen in Fig. 3, yields a product which is close to $YBa_2Cu_3O_7$ in formula.

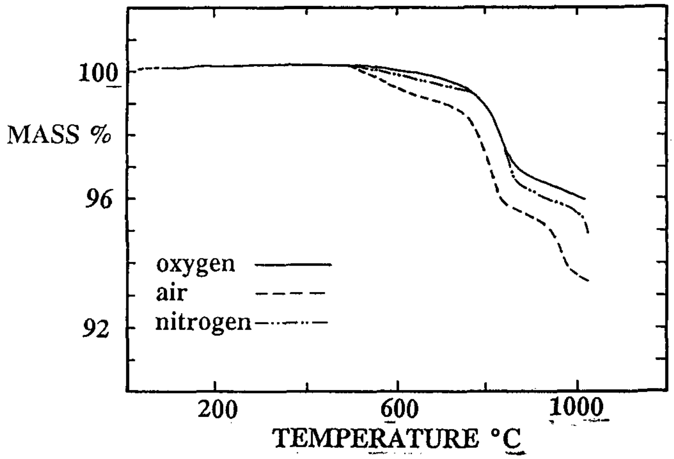

Fig. 4 TG data for the heating of YBCO in oxygen, air and nitrogen. (Heating rate 5 deg·min^{-1}) (After Lau *et al.* [12])

The take-up of oxygen during the cooling cycle from sintering temperatures is perhaps the most critical stage of the preparation of YBCO superconductors.

Many thermogravimetric studies have been made of this phenomenon. Most studies have focussed on the mass gain aspects of the oxygen take-up in an attempt to evaluate the oxygen diffusion within the material [10, 11].

However, if mass loss is considered in more detail, it is clear from the work of Irvine *et al.* [8] and Lau *et al.* [12] that two oxygen diffusion processes must exist to account for the observed thermogravimetric data. Figure 4 shows TG data obtained on heating superconducting material of composition close to $YBa_2Cu_3O_7$, in oxygen, air and nitrogen at 5 deg·min^{-1} [12]. The shapes of these TG curves indicates that oxygen is not lost in a simple, single-stage process. The explanation for these data is that the transition from the superconducting, orthorhombic $YBa_2Cu_3O_{7-\delta}$ phase to the semiconducting, tetragonal phase, which occurs as oxygen is lost, becomes a contributor to oxygen diffusivity. Figure 5 shows how this may occur. On heating, the orthorhombic phase can lose oxygen according to route k_{-4}, to yield an orthorhombic, oxygen-deficient material, or it may undergo a phase transition to the tetragonal form as, indicated by route k_b, which then continues to lose oxygen. The oxygen-deficient orthorhombic material produced by route k_{-4} subsequently undergoes a phase transition to give the tetragonal phase, so the end result of the two routes is the oxygen-deficient tetragonal phase. According to Lau *et al.* [12] the orthorhombic/tetragonal transition occurs at the relatively high temperature of approximately 625°C. Consequently, at temperatures of the order of 600°C and below, the loss of oxygen occurs via route k_{-4}. However, at temperatures of 600°C and above, a new route becomes important, namely that given by k_b in Fig. 5, such that oxygen loss occurs via k_{-5} as shown on Fig. 5. The end result is that a different diffusion process is involved at the higher temperatures, which gives a different overall rate of mass loss, as observed in the work of both Irvine *et al.* [8] and Lau *et al.* [12].

$$\begin{tikzcd}
YBa_2Cu_3O_{7-\delta} + O_2 \arrow[rr, shift left, "k_4"] & & YBa_2Cu_3O_{7-\delta} \arrow[ll, shift left, "k_{-4}"] \\
\text{(orthorhombic)} \arrow[d, "k_a"] & & \text{(orthorhombic)} \arrow[d, "k_b"] \\
YBa_2Cu_3O_{7-\delta} + O_2 \arrow[rr, shift left, "k_5"] & & YBa_2Cu_3O_{7-\delta} \arrow[ll, shift left, "k_{-5}"] \\
\text{(tetragonal)} & & \text{(tetragonal)}
\end{tikzcd}$$

Fig. 5 Schematic showing possible routes for oxygen loss from YBCO superconductor. (After Lau *et al.* [12])

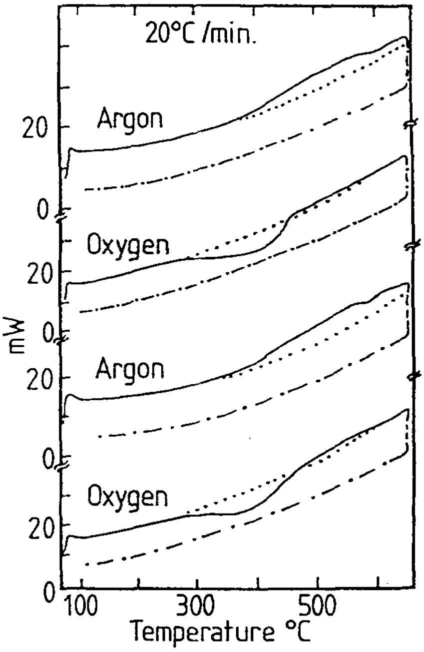

Fig. 6 DSC traces from successive heating of YBCO from 70 to 650°C at 20 deg·min^{-1}. (a) and (c) were run in argon, (b) and (d) in oxygen. (After Glowacki *et al.* [13])

The re-oxygenation of YBCO materials has also been studied by DSC [13]. Figure 7 shows successive DSC traces obtained on heating from 70 to 650°C in alternate oxygen and argon atmospheres. Heating in argon yielded an endothermic peak at approximately 300 to 450°C, which was attributed to oxygen loss. Subsequent heating in oxygen gave a broad exothermic peak over the range 350 to 650°C, which was attributed to the reoxygenation process.

In an attempt to overcome the problems associated with oxygen content in $YBa_2Cu_3O_{7-\delta}$ superconductor some recent work has focussed on to an YBCO material having the composition $YBa_2Cu_4O_8$ as this appears to have higher oxygen stability. Both DTA and TG have been used to study this material. Figure 7 shows DTA data for the heating of $YBa_2Cu_4O_8$ in O_2 at a rate of 10 deg·min^{-1}, as determined by Ravichandran *et al.* [14]. It can be seen that the compound exhibits four endothermic reactions with onset temperatures of 897, 925, 958 and 986°C. The endotherms at 897, 925 and 986°C are small whilst that at 958°C is large. At 897°C the 124 compound is stated to decompose to $YBa_2Cu_{3.5}O_{7.5}$ and CuO. At 925°C the new compound, $YBa_2Cu_{3.5}O_{7.5}$, decomposes to give tetragonal 123 and CuO. The major even at 958°C is attributed to a peritectic reaction between 123 and CuO which yields Y_2BaCuO_5 (211) and a liquid phase. The final event at 986°C was explained by the occurrence of incomplete peritectic reaction at 958°C, which on further heating allows unreacted CuO to react peritectically with the 211 phase to give $Y_2Cu_2O_5$ and a liquid phase. This latter reaction was also observed by Aselage and Keefer [15] at 975°C in air and was stated to occur at higher temperatures in oxygen.

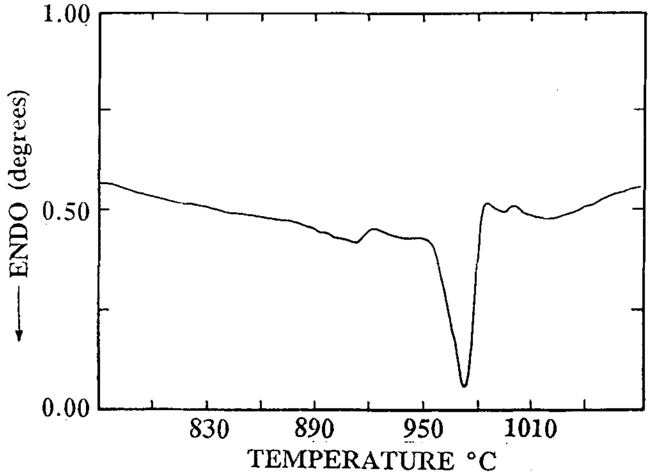

Fig. 7 DTA trace for $YBa_2Cu_4O_8$ sample heated in O_2 at 10 deg·min^{-1} (After Ravichandran *et al.* [14])

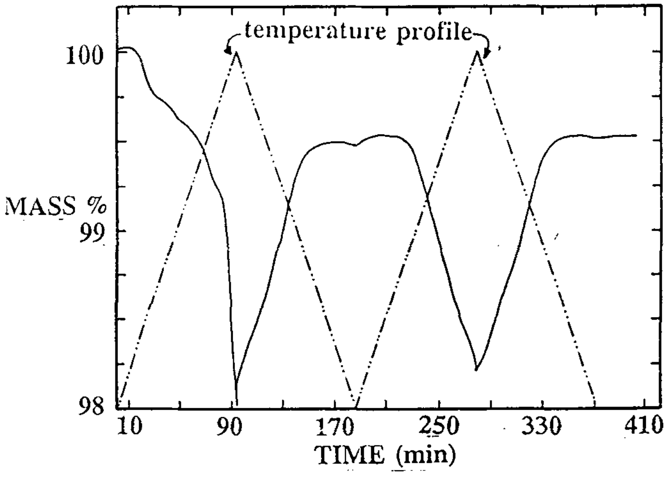

Fig. 8 TG data obtained on repeated heating and cooling of an initial sample of $YBa_2Cu_4O_8$, dotted line is the temperature profile. (After Ravichandran *et al.* [14])

To test the reversibility, or otherwise, of oxygen loss on heating of the 124 phase, Ravichandran *et al.* [14] cycled the phase between 50 and 980°C in O_2 in a thermobalance to give the data shown in Fig. 8. The initial mass loss of approximately 1.95% was explained by the decomposition of 124 to give tetragonal 123 and CuO with the evolution of oxygen. During cooling oxygen is taken into the tetragonal 123 phase to give the superconducting orthorhombic 123 phase, with an associated mass increase of the order of 1.44%. It is clear that reaction does not occur between the 123 phase and CuO to re-form the 124 phase. Subsequent cycling showed the reversibility of oxygen uptake and loss from the 123 phase. It is, however, clear that the 124 phase cannot be cycled reversibly.

From the data presented briefly in this subsection, along with that given in section 2.1, it is clear that a wide range of thermoanalytical methods can be used to determine important effects associated with both the calcination and sintering stages of conventional ceramic processing.

Citrate gel processing

As indicated earlier citrate gel processing is one example of a range of alternative processes for the production of particulate materials [16]. The reasons for such processes may be summarised as control of chemical homogeneity, control of particle size, control of morphology and control of purity. The most promising methods, which use solutions as the basic feed, are precipitation processes, gel processes, freeze-drying and hydrothermal processes. Whilst the understanding of each of these processes can be improved by the use of thermoanalytical techniques, the present paper will concentrate on the use of thermal analysis in citrate gel processing as one example of the rapidly growing field of the gel processing of ceramic materials.

As with many alternative ceramic production processes, the aims of citrate gel processing may be summarised as the preservation of the homogeneity of an aqueous solution in the solid state. In citrate gel processing this is achieved by the formation of a gel in which citrate and nitrate ions are complexed together with all the required metallic ions. Once the ions are complexed within the gel, a drying process is used at approximately 85°C to produce a stable dried precursor [17]. To produce the ceramic, decomposition/oxidation of the gel precursor is needed. It is at this stage that the use of thermal analysis becomes of great importance so that the thermal stability of the gel precursor and the decomposition mechanism of the precursor may be determined. Without this knowledge complete control of the production of the ceramic phase is impossible. Once the ceramic phase has been obtained, thermal analysis offers a means of studying subsequent processing, as in the conventional route.

The potential difficulties that may be encountered in the use of any gel processing operation are concerned with the crystallisation of phases during gel production, as this may introduce unacceptable inhomogeneity into the solid;

segregation or loss of elements during the decomposition/oxidation of the precursor, as these would change homogeneity and stoichiometry of the solid; and formation of agglomerates in the particulate solid during decomposition/oxidation of the gel precursor, as this may alter the sinterability of the powder and cause high levels of porosity in the final ceramic product. Thermal analysis techniques can give data which can help obviate or solve these difficulties.

The decomposition/oxidation of citrate-gel precursors has been studied for a number of materials [17–19]. Two types of pyrolysis reactions have been observed. Type I was characterised by a continuous and vigorous reaction and often occurred with precursors containing Fe, Ni, Ag, Cu and Co, which have a catalytic activity in oxidation processes. Such behaviour has also been observed in gel precursors that contain ammonium nitrate, which decomposed on heating to provide oxidants to help in the decomposition/oxidation of the organic component of the gel precursors [20]. Type II pyrolysis was characterised by a multistage decomposition in which intermediate decomposition steps occurred, which were associated with the formation of transiently-stable compounds within the semi-decomposed precursors. Often the compounds were mixed citrate salts. Ideally, type I pyrolysis is favoured in a ceramic powder production process because there is little chance of the occurrence of chemical heterogeneity during pyrolysis. In type II pyrolysis there is the possibility that the formation of transiently-stable compounds can cause inhomogeneity if sufficiently large crystals of the compounds are produced.

As the decomposition/oxidation process of the gel involves considerable change in mass and the evolution of gases it is evident that both TG and EGA offer convenient techniques for the study of the reactions involved. There is also a considerable enthalpic effect during the decomposition/oxidation process, which makes both DTA and DSC excellent experimental methods for use in studies of these processes.

Production of soft ferrites

MgO-based soft ferrites have been produced using the citrate gel process [21]. TG data for the decomposition/oxidation of the gel precursor are given in Fig. 9, where it can be seen that the decomposition followed an 'almost ideal' type I pyrolysis behaviour. A rapid mass loss commenced at approximately 200°C and was almost completed by 400°C. Further mass losses, due to the removal of residual carbon, were small and were completed by 700°C. On the basis of this data, and DTA data, which showed the pyrolysis to be extremely exothermic, a two stage decomposition/oxidation procedure was adopted for the production of ceramic powders from the precursors. A low temperature stage at 250–300°C was used to initiate decomposition without excess overheating so that ZnO loss would not occur from the ferrite. Higher temperatures of 700, 900 and 1100°C were used as different second stage temperatures with calcination periods of 2 h to fully decompose/oxidise the precursor and to control the formation and grain size of the ferrite. Slight increases in mass loss were associated with increases in the temperature of the second stage as the residual carbon content decreased from 0.07 wt% at 700°C, to 0.06 wt% at 900°C and 0.02 wt% at 1100°C [21].

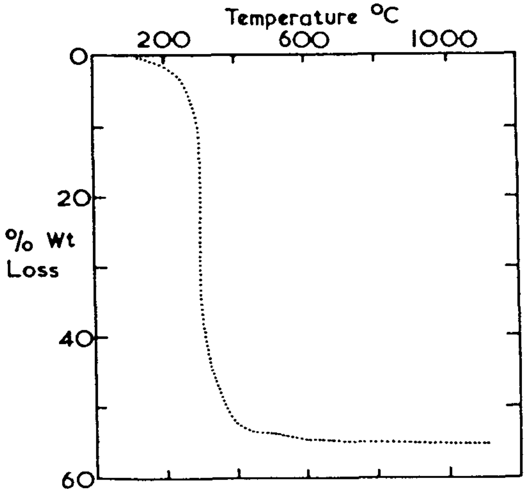

Fig. 9 TG data for the decomposition/oxidation of gel precursor of MgO-based ferrite. (Air atmosphere, heating rate 10 deg·cm^{-1})

Dilatometric traces for powders produced by the two-stage processing route are given in Fig. 10. It is evident that as the temperature of the second stage of pyrolysis is increased, the reactivity of the powders decreases with the result that the onset of sintering is moved to higher temperatures. This behaviour reflects the particle size of the ferrite powders obtained at the different temperatures. The sub-micron powders produced at 300–700°C begin to densify at 690°C. It is interesting to note the inflexion in the sintering curve for this powder at a temperature of approximately 900°C. Microstructural examination of pellets, before and after this temperature region, indicated that grain growth, rather than densification, began to occur at temperatures in excess of 900°C.

A comparison of the sintering behaviour of the 300–700°C powder with that of a commercial spray-dried, precalcined powder and an industrial dry-granulated powder, all of the same composition, is given in Fig. 11 which shows remarkable differences between the powders. It is evident that the dry-granulated powder is not fully reacted to form the ferrite, hence the expansion at temperatures in the range 600 to 950°C. The gel processed powder and the pre-calcined

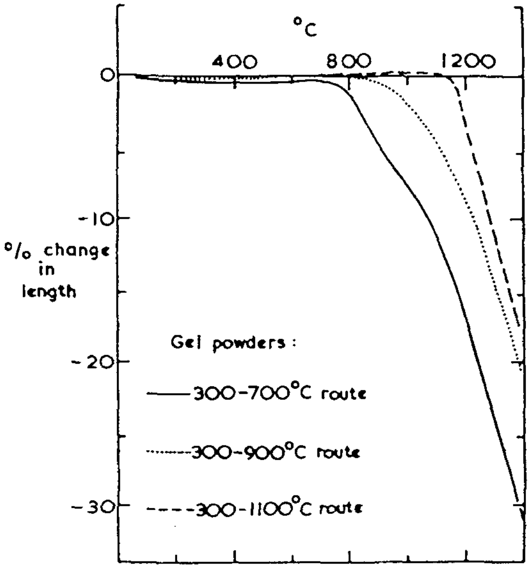

Fig. 10 Dilatometric traces for sintering of MgO-based soft ferrites produced by gel pyrolysis. (Air atmosphere, heating rate 20 deg·min^{-1})

powder can both be seen to be fully reacted before sintering began. An added benefit of the gel processed material was the controlled uniform grain size that was obtained, relative to the duplex structure which tends to result with the commercial samples. The controlled grain size resulted in lower power losses in these ferrites [22].

Production of Y–Ba–Cu–O superconductor

Figure 12 shows TG data for the decomposition/oxidation of gel precursors of the high T_c superconductors $La_{1.7}Sr_{0.15}Ba_{0.15}CuO_4$ and $YBa_2Cu_3O_{7-delta}$ [23]. It is evident that the two precursors decompose/oxidise in different manners. The precursor of the La-based superconductor decomposed in a single-stage, type I pyrolysis once dehydration was complete at approximately 150°C. The precursor of the 123 Y-based superconductor decomposed in two quite separate stages, which indicated either a type II pyrolysis or that a crystalline phase had precipitated during gel production. X-ray diffraction of samples of the precursor, heated to temperatures before and after the step in the TG curve, showed the existence of barium nitrate. Thus it was clear that at the higher barium content of the 123 YBCO superconductor, relative to the $La_{1.7}Sr_{0.15}Ba_{0.15}CuO_4$ material, all the barium nitrate could not be retained in solution during gel production because of its low solubility in water. It was subsequently shown that control of *pH* at 6 using ammonium hydroxide additions prevented the precipitation of barium nitrate during gel production and the subsequent pyrolysis process became a single stage, type I reaction.

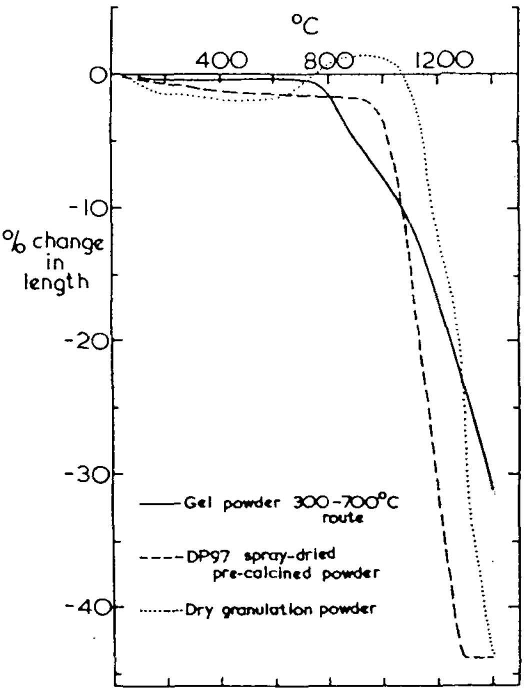

Fig. 11 Dilatometric traces for sintering of MgO-based soft ferrite produced by gel pyrolysis, spray drying of pre-calcined powder and dry granulation processes. (Air atmosphere, heating rate 20 deg·min^{-1})

Further evidence for the conclusion that the step in Fig. 12 was the result of the presence of barium nitrate and not the transient existence of a metastable mixed citrate salt became apparent in TG studies of precursors in which Ho and Eu were substituted for Y in the 123 superconductor and for one in which Eu was substituted for both Y and Ba. The TG data from these studies are presented in Fig. 13. In the former cases the step is still present because of the presence of Ba as the nitrate salt, whereas in the latter case the step is absent because Eu has been substitued for both Y and Ba in the superconductor.

Sintering studies of powders produced using similar two-stage processing to that described in section 3.1 for ferrites confirmed the dependence of the temperature of the onset of densification on processing temperature (Fig. 14). An interesting observation from the data shown in Fig. 14 was that as soon as the maximum temperature was reached, shrinkage of the superconducting pellet

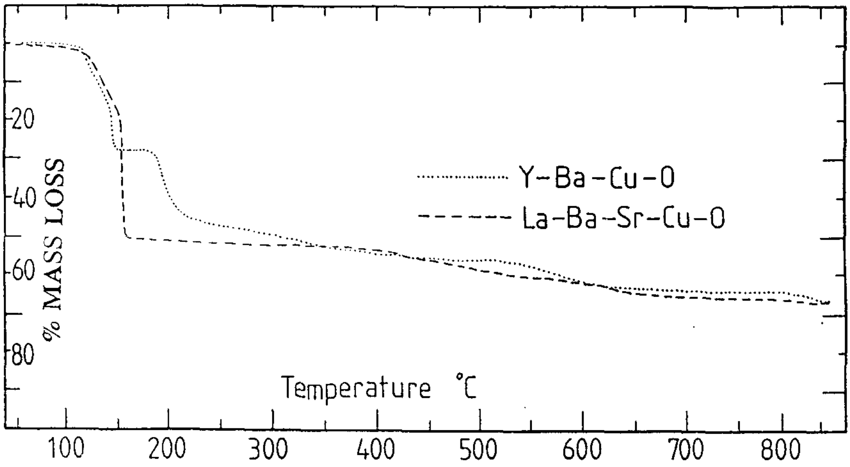

Fig. 12 TG data for pyrolysis of La and Y-based precursors of high T_c superconductors. (Air atmosphere, heating rate 10 deg·min^{-1})

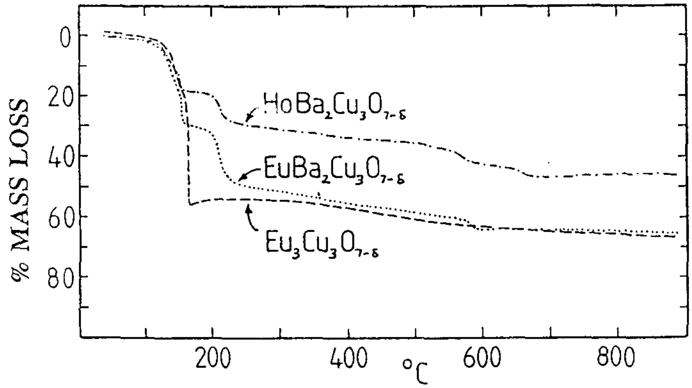

Fig. 13 TG data for pyrolysis of Ho and Eu-based precursors of 123 superconductors. (Air atmosphere, heating rate 10 deg·min^{-1})

ceased. These data were determined in air. If, however, the dilatometry was conducted in oxygen it was found that isothermal sintering occurred at the maximum temperature reached, as indicated in Fig. 15. These data showed the importance of atmosphere upon the sintering behaviour of YBCO superconductors.

In section 2.2 it was shown that the take-up of oxygen after sintering by the YBCO material was important for the production of an orthorhombic superconducting sample. During dilatometric studies of the gel-processed samples, in which samples were allowed to cool in a controlled manner (1.5 deg·min^{-1}) in

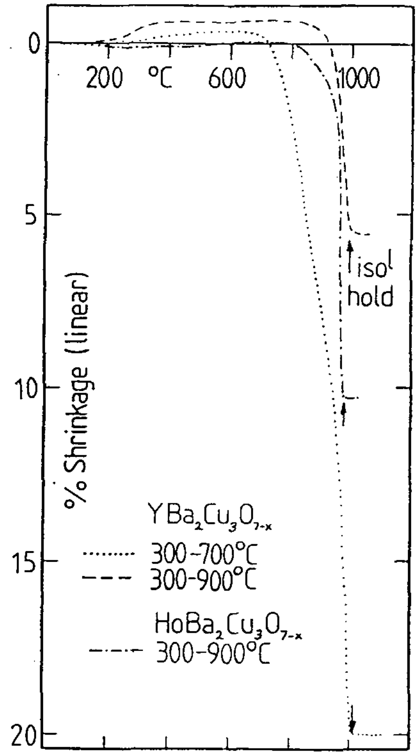

Fig. 14 Dilatometric traces for sintering of powders of Y-based and Ho-based superconducting 123 materials. (Air atmosphere, heating rate 10 deg·min^{-1})

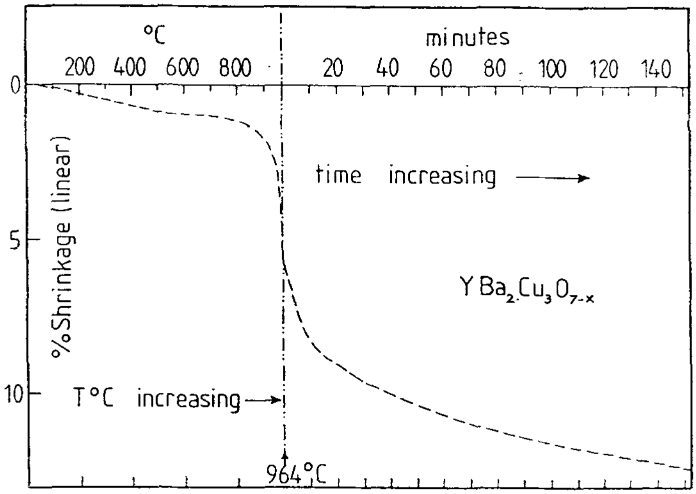

Fig. 15 Dilatometric trace for YBCO superconductor powder compact in oxygen showing isothermal hold at maximum temperature. (Heating rate 10 deg·min^{-1})

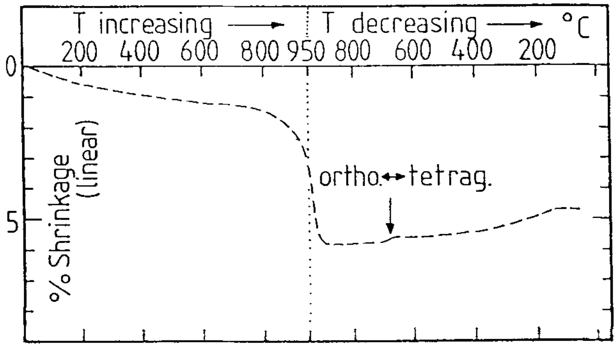

Fig. 16 Dilatometric trace for YBCO superconductor showing heating (10 deg·min^{-1}) and cooling (1.5 deg·min^{-1}) in oxygen

oxygen, it was shown that take-up of oxygen and the tetragonal to orthorhombic transition could both be detected, as shown in Fig. 16. These data agree well with the other re-oxygenation measurements made using TG and DSC, as described in section 2.2, and indicate the usefulness of dilatometry in the study of such reactions.

Concluding comments

The aim of this paper has been to show how thermoanalytical techniques may be used to advantage in studies of the processing of magnetic and electronic ceramics. The examples of soft ferrites and YBCO high T_c superconductors have shown how TG, DTA, DSC and dilatometry may be used in studies of both conventional ceramic processing methods and gel processing techniques. It is hoped that these examples will lead other investigators to use this range of techniques in future studies of electronic and magnetic ceramics. The present day convenience of modern instruments, the ease of operation of data-processing systems and the extended working temperature ranges which are now available, make these thermoanalytical methods vital yet convenient for studies of this rapidly growing class of ceramic materials.

* * *

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Zusammenfassung — Sowohl in herkömmlichen Keramikverfahren als auch in den neuartigen Gelverfahren ist die Kontrolle der Fertigungsparameter für die Produktion von elektronischen und magnetischen Keramikstoffen von entscheidender Bedeutung. Es wird die Rolle der Thermoanalyse bei der Ermittlung von Daten zum besseren Verständnis beider Herstellungsverfahren diskutiert und dabei besonderer Bezug auf die Fertigung von 1-2-3 YBCO Supraleitern und von Weichferritmaterialien auf MgO-Unterlage für die Anwendung in TV-Ablenkungseinheiten genommen.