

Preparation of alkaline earth carbonates and oxides by the EDTA-gel process

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The ethylene-diamine-tetra-acetic acid (EDTA)-gel process has been used to produce carbonates and oxides of the alkaline earth elements Ba, Sr and Ca and their solid solutions. These materials have a range of potential applications including electron emission and catalysis. Gels of composition Ba-EDTA, Sr-EDTA, $[\text{Ba}_{0.5}\text{Sr}_{0.5}]$ -EDTA, $[\text{Ba}_{0.5}\text{Sr}_{0.45}\text{Ca}_{0.05}]$ -EDTA were prepared at pH 6 from aqueous solutions of the alkaline earth nitrates and EDTA and their thermal decomposition studied by TGA/DSC. The gels and the products derived from calcination of these gels at different temperatures have been characterised by FTIR, XRD and SEM, and shown to have high chemical homogeneity and fine particle size. Decomposition of the gels to the carbonate form occurred below 300°C with subsequent formation of the oxide occurring on heat treatment at temperatures ranging from approximately 800°C to >1000°C depending upon gel composition. The process route is suitable for the production of particulate materials or porous coatings.

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1. Introduction

The unusual chemical and electrical properties of alkaline earth oxides and their carbonate precursors give rise to their current or potential use in range of specialist applications. Apart from their use as a constituent of systems such as high temperature superconductors, ferroelectrics and fuel cells, alkaline earth oxides, in particular those of barium, strontium and calcium, are of particular value used either individually or in combination as the active component of low work function sources for electron emission [1] and as catalysts for a range of processes [2, 3]. The requirements of these applications generally include high surface activity/small particle size, good chemical homogeneity, the ability to form thin films or surface coatings and chemical stability during processing. The last of these requirements precludes the use of conventional sol-gel processing routes, which would otherwise seem to be an attractive option, due to the hygroscopic nature of the oxides, and processing of these materials is normally based on the use of carbonate precursors which are decomposed in situ to form the oxide.

Alkaline earth carbonates are most commonly prepared by precipitation routes involving reaction of the alkaline earth nitrates with sodium or ammonium carbonates [4], however these processes suffer from a number of problems. In particular contamination of the alkaline earth carbonates occurs by insoluble residual nitrates formed as a by product of the reaction. In

addition the particle size of the precipitates produced by these processes tends to be relatively coarse [4]. An alternative process route which could avoid these problems would be attractive.

The aqueous organic gel route, was originally developed by Pechini [5] and Marcilly and co workers [6]. The process involve the aqueous reaction of single or multiple metal nitrate precursors with a polyfunctional acid such as citric acid, to produce stable complexes and prevent precipitation allowing the production of an amorphous gel on drying, which can be subsequently decomposed to the metal carbonates or oxides on thermal treatment. In comparison with conventional sol-gel processing routes based on alkoxides, the technique requires inexpensive precursors, allows the use of an aqueous based processing system and results in the formation of the oxides on heating, sometimes via (atmospherically stable) carbonate intermediates.

Although organic gel complex processing routes have been previously used to produce multicomponent oxide systems containing alkaline earth constituents [7–9], the processing and properties of single or mixed alkaline earth carbonates or oxides prepared by this route has not been previously reported. The aim of this investigation was therefore to determine the feasibility of utilising such a process route to produce these materials and to investigate the processes of gel conversion and properties of the resultant carbonate and oxide products.

2. Experimental procedure

2.1. Preparation of the precursors

The starting reagents used were AnalaR grade Ba(NO₃)₂, Sr(NO₃)₂, Ca(NO₃)₂ · 4H₂O, EDTA, and 35% ammonia solution all supplied by BDH/Merck. The alkaline earth nitrate salts were separately dissolved in deionised water and diluted to form 0.1 M aqueous precursor solutions. A 0.1 M EDTA solution of pH 6 was also prepared by dissolving the requisite quantity of EDTA in deionised water whilst adding the required amount of ammonia solution to achieve the desired pH.

According to the composition required, one or more of the metal salt solutions were then gradually added to the EDTA solution with continuous magnetic stirring to give a solution of equal molar ratio of metal ions: EDTA. The pH of the solution was continually monitored and maintained at a value of 6 by further addition of the ammonia solution as required. The final solution was stirred magnetically at room temperature for 4 h to equilibrate after which time it was transferred to a rotary evaporator and evaporated under a vacuum at 60–70 °C to remove surplus water until a viscous liquid was obtained. The resultant viscous liquid was then poured into an evaporating basin and heated in a vacuum oven at 80 °C for 10 h to produce a solid precursor or could be used directly for the production of (porous) coatings by the use of spraying or dip coating techniques.

In order to demonstrate the application of the process for the production of a range of alkaline-earth carbonates and oxides, the following compositions were prepared as model systems; Ba-EDTA, Sr-EDTA, Ca-EDTA, Ba_{0.5}Sr_{0.5}-EDTA, Ba_{0.5}Sr_{0.45}Ca_{0.05}-EDTA. The last two multi-component compositions are precursors to typical mixed oxide compositions used in electron emission sources such as the oxide cathode.

2.2. Thermal decomposition and characterisation of the precursors and resultant products

The decomposition processes of the as-prepared precursors were investigated by Thermo-Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC), using Mettler TG50 and DSC30 instruments to a maximum temperature of 1000 °C and 600 °C respectively.

The structure, composition and morphology of the precursors and the products derived from their thermal treatment at different were examined by: X-Ray Diffraction (XRD) using a Philips 1050 diffractometer (Cu K_α radiation); Fourier Transform InfraRed Spectroscopy (FTIR) using a Mattson 3000 FTIR spectrometer, and Scanning Electron Microscopy (SEM) using a Cambridge S360 instrument.

The thermal treatments for all the results reported were carried out in air, with a heating rate of 10 °C/minute and a dwell time at the maximum temperature of 1 hour. The dried gels and products derived from their calcination were friable in nature and were easily crushed to facilitate the analyses, with the samples for microstructural examination being prepared by dis-

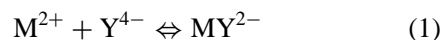
persing the resultant powders in ethanol and dropping this onto the aluminium microscope stub prior to the application of a conductive gold coating. FTIR analysis was also performed on the crushed material using the KBr disc method.

3. Results and discussion

3.1. Gel formation

Aqueous organic gel processing routes most commonly utilise citric acid as the complexing agent. However, there are practical difficulties associated with the use of citric acid, particularly in the case of strontium containing gels which have been found to undergo phase separation and precipitation of strontium nitrate due to the limited stability of these complexes.

EDTA (CH₂N)₂(CH₂COOH)₄ is a well-known poly-functional hydroxylic acid which forms stable soluble complexes with most metallic elements, and which can be used to produce inorganic oxides by an aqueous organic gel route similar to the citrate-gel process [7–10]. In comparison with the citrate-gel process, the metal complexes formed with EDTA are more stable and soluble. EDTA is known to form complexes with the alkaline earth metal ions, for which it is often used in complexometric titrations in analytical chemistry [11–13], and it was therefore decided to standardise on the use of EDTA as the complexing agent for the production of all the systems investigated in this work. The complexing reactions for divalent metal ions such as the alkaline earth metals are of the form:



Where Y⁴⁻ = (CH₂N)₂(CH₂COO)₄⁴⁻ And the formation constant for reaction (1) is given by:

$$K_f = [MY^{2-}] / [M^{2+}][Y^{4-}] \quad (2)$$

The formation of the organometallic complexes and the nature of the resultant gels and their decomposition depends on pH. In aqueous solution, EDTA can remain as the compound H₄Y or disassociate increasing numbers of protons to form the species H₃Y⁻, H₂Y²⁻, HY³⁻ or Y⁴⁻ with the proportions of these species varying with pH [11]. Stable chelates are formed with the Y⁴⁻ species, with the stability of these chelates affecting the equilibrium between the variously deprotonated species of EDTA [12]. Generally, the minimum pH value at which MY⁴⁻ complexes are formed increases with decreasing stability of the chelated ion. In addition, the solubility of EDTA, which is very limited in aqueous solutions increases with increasing pH [13].

To facilitate the formation of stable EDTA solutions and complexes, ammonia additions were used in this work as an easily removed pH modifier.

A secondary but important effect of these additions is to produce ammonium nitrate by reaction of the ammonia with the NO₃ groups from the alkaline earth nitrate precursors. This compound is strongly oxidising and greatly accelerates the decomposition of the gel precursors on heating, producing strongly exothermic

reactions [10, 14]. These reactions can result in coarsening of the resultant particles due to the generated heat [10, 14], the destruction of coatings produced using these products due to the generation of gaseous reaction products, and in extreme cases may result in explosive reactions [15]. Consequently, the addition of excess ammonia is generally deleterious and to be avoided in aqueous organic gel process routes.

The pH value of 6 which was used in the gel processing route for these materials was chosen as the lowest pH value (and hence ammonia addition) which would be anticipated to result in substantial complexation reactions for all of the alkaline earth elements used. The value was determined by calculation of the conditional formation constant K_{cf} for the EDTA-Alkaline earth complexes where K_{cf} represents the modified formation constant for the complexation reaction given in Equation 1, taking into account the competing reactions for the formation of the alternatively protonated forms of EDTA as a function of pH according to the following:

$$K_{cf} = \alpha_4 K_f \quad (3)$$

$$\frac{1}{\alpha_4} = 1 + \frac{[H^+]}{K_{a4}} + \frac{[H^+]^2}{K_{a3}K_{a4}} + \frac{[H^+]^3}{K_{a2}K_{a3}K_{a4}} + \frac{[H^+]^4}{K_{a1}K_{a2}K_{a3}K_{a4}} \quad (4)$$

Where α_4 is the fraction of the total EDTA species that exists as Y^{4-} at a given pH and hence $[H^+]$, K_{ai} ($i = 1, 2, 3, 4$) are the dissociation constants of the variously protonated H_3Y^- , H_2Y^{2-} , HY^{3-} or Y^{4-} forms of EDTA in aqueous solution, with the values 1.0×10^{-2} , 2.2×10^{-3} , 6.9×10^{-7} and 5.5×10^{-11} respectively [11].

The calculated values of K_{cf} for various pH values are shown in Table 1 for Ba, Sr and Calcium EDTA complexes. These data show that the conditional formation constant and stability of Barium EDTA complexes is lowest of these alkaline earth complexes for a given pH and that the value of K_{cf} increases significantly between pH 5 and 6. It should be noted that in contrast to complexometric titrations with EDTA, in which a high value of K_{cf} (normally $>10^6$) is essential to provide a distinct end point [13], a lower value of the conditional formation constant for complex formation may be acceptable in EDTA gel processing routes, in which the requirement is simply for the EDTA complexes to remain intact during dehydration and gel formation.

TABLE I Conditional formation constant K_{cf} of M-EDTA in different pH

pH	α_4	Ba-EDTA	Sr-EDTA	Ca-EDTA
10	3.5×10^{-1}	2.01×10^7	1.49×10^8	1.75×10^{10}
9	5.2×10^{-2}	2.99×10^6	2.22×10^7	2.61×10^9
8	5.4×10^{-3}	3.11×10^5	2.30×10^6	2.71×10^8
7	4.8×10^{-4}	2.76×10^4	2.04×10^5	2.40×10^7
6	2.2×10^{-5}	1.27×10^3	9.37×10^3	1.1×10^6
5	3.5×10^{-7}	2.01×10	1.49×10^2	1.75×10^4
4	3.6×10^{-9}	2.07×10^{-1}	1.53×10^0	1.80×10^2

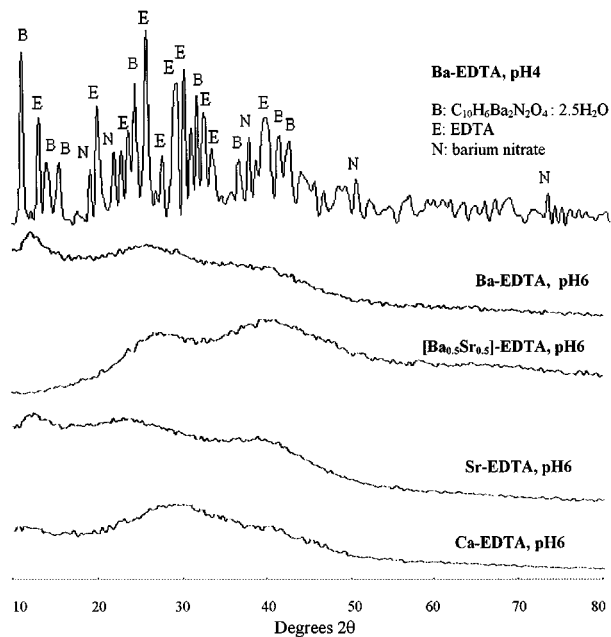


Figure 1 XRD patterns obtained from the alkaline-earth EDTA gels of various composition and pH after drying at 80°C under vacuum. NB different intensity scales used for amorphous and crystalline samples for clarity.

The typical XRD patterns of the dried Ba-EDTA, Sr-EDTA, Ca-EDTA and $[Ba_{0.5}Sr_{0.5}]$ -EDTA complexes are shown in Fig. 1. The XRD patterns indicate that these solid products are essentially amorphous gels, confirming the effectiveness of the complexation at pH 6. There is some evidence of embryonic crystallisation, but this is not significant with regards to the effectiveness of the gel process route.

The effect of lower additions of ammonia and hence pH values in the solution is also shown in Fig. 1, which shows the XRD pattern obtained after drying a Ba-EDTA complex solution prepared at pH 4. In this case, the XRD pattern is characteristic of a mixture of uncomplexed EDTA (E) [16] and barium nitrate (B) [17] together with a crystalline phase identified as barium ethylenetetraacetate hydrate [18] indicating that incomplete complexation of the metal ions took place at this pH value. The formation of a crystalline complex phase in this case is believed to be due to a seeding effect of the Barium Nitrate and/or EDTA crystals formed at this pH value.

The FTIR spectra for the dried Ba-EDTA and Sr-EDTA precursors are shown in Fig. 2. The bands of

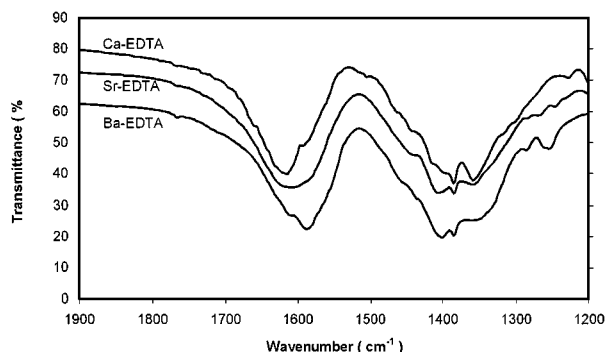


Figure 2 FTIR data showing the formation of the alkaline earth-EDTA complexes.

1585 cm^{-1} for the Ba-EDTA precursor and 1630 cm^{-1} for the Sr-EDTA precursor can be attributed to asymmetrical stretching of $-\text{COO}^-$ groups deriving from the acid groups in the EDTA bound to the metal ions [19], confirming the formation and retention of alkaline earth/EDTA complexes in these gels. In addition, bands at 1356 and 1410 cm^{-1} can be attributed to the characteristic frequencies of the $-\text{NO}_3^-$ group [19] of the nitrate existing in the precursors, most probably in the form of NH_4NO_3 since no crystallisation of uncomplexed $\text{Ba}(\text{NO}_3)_2$ or $\text{Sr}(\text{NO}_3)_2$ was apparent in the XRD patterns for these samples.

3.2. Thermal decomposition and formation of carbonate and oxide products

The results of the DSC, TGA, FTIR and XRD studies of the structural and chemical changes occurring

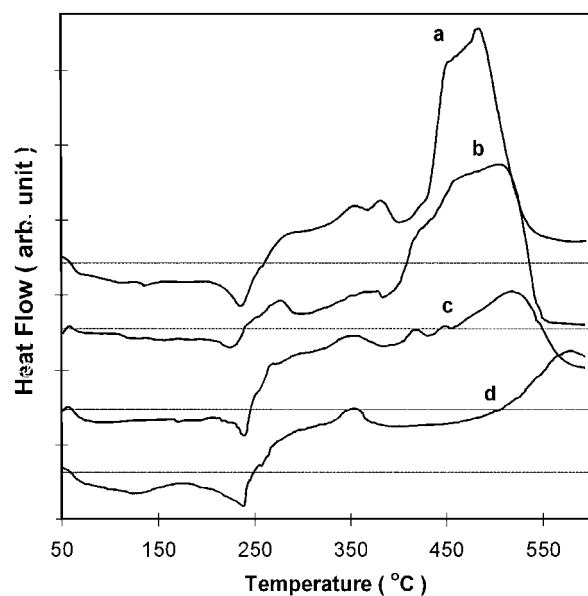


Figure 3 DSC results for the temperature range 20–600°C showing the decomposition of the gels of composition: (a) $[\text{Ba}_{0.5}\text{Sr}_{0.5}]$ -EDTA, (b) Ba-EDTA, (c) Sr-EDTA, (d) Ca-EDTA.

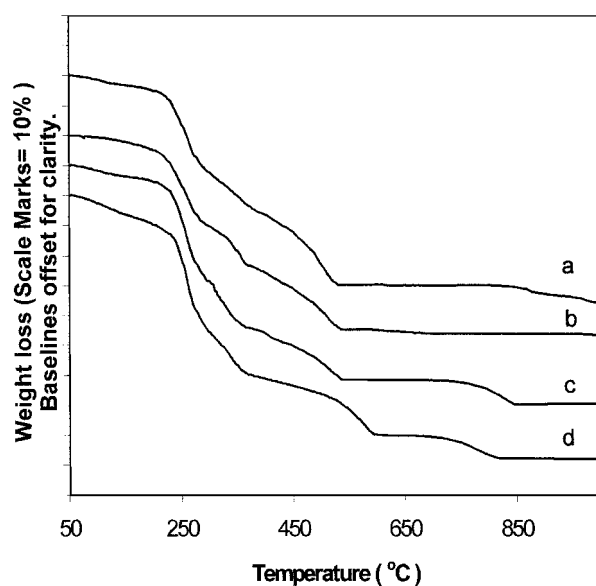


Figure 4 TGA analysis results over the range 50–1000°C for the gels of composition: (a) $[\text{Ba}_{0.5}\text{Sr}_{0.5}]$ -EDTA, (b) Ba-EDTA, (c) Sr-EDTA, (d) Ca-EDTA.

during thermal decomposition of the gels are shown in Figs 3–7 for Ba-EDTA, Sr-EDTA, Ca-EDTA and $[\text{Ba}_{0.5}\text{Sr}_{0.5}]$ -EDTA gels. The results show that decomposition occurs by a four-stage process, with similar behaviour for all the compositions investigated, but with the temperatures corresponding to the various stages depending upon the gel composition. These are discussed in more detail below.

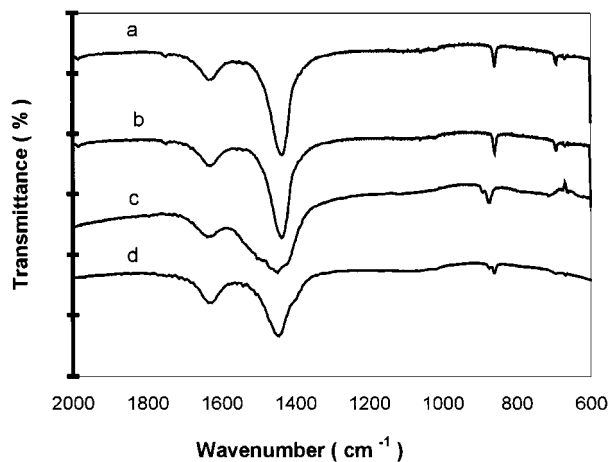


Figure 5 FTIR spectra of the powders derived from calcination of different gels at 300°C: (a) Ba-EDTA gel, (b) Sr-EDTA gel, (c) $[\text{Ba}_{0.5}\text{Sr}_{0.5}]$ -EDTA gel and (d) Ca-EDTA gel.

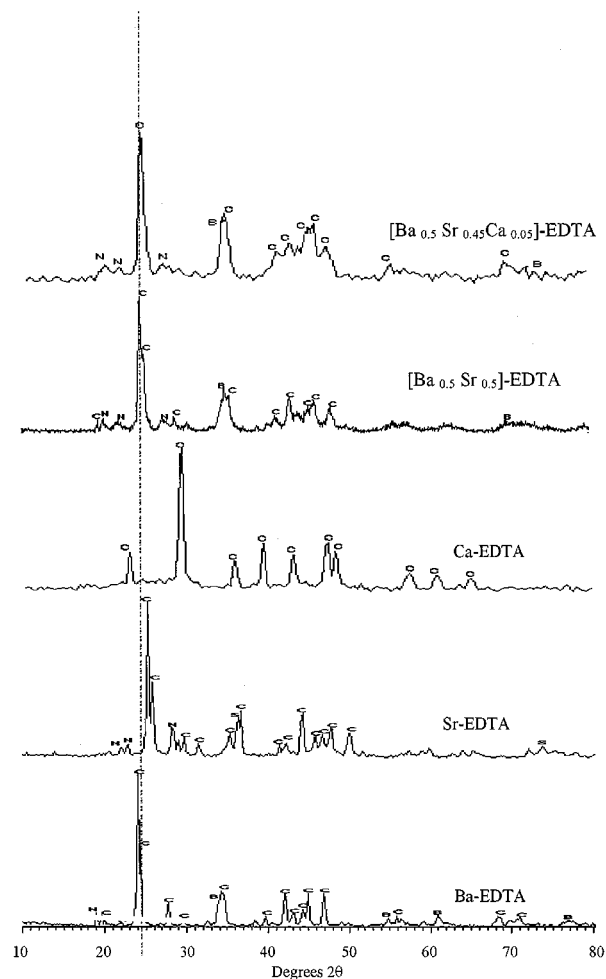


Figure 6 XRD patterns of the powders derived from calcination of different gels at 300°C (Peak assignments - C: carbonates, B: barium oxide, S: strontium oxide, N: nitrates).

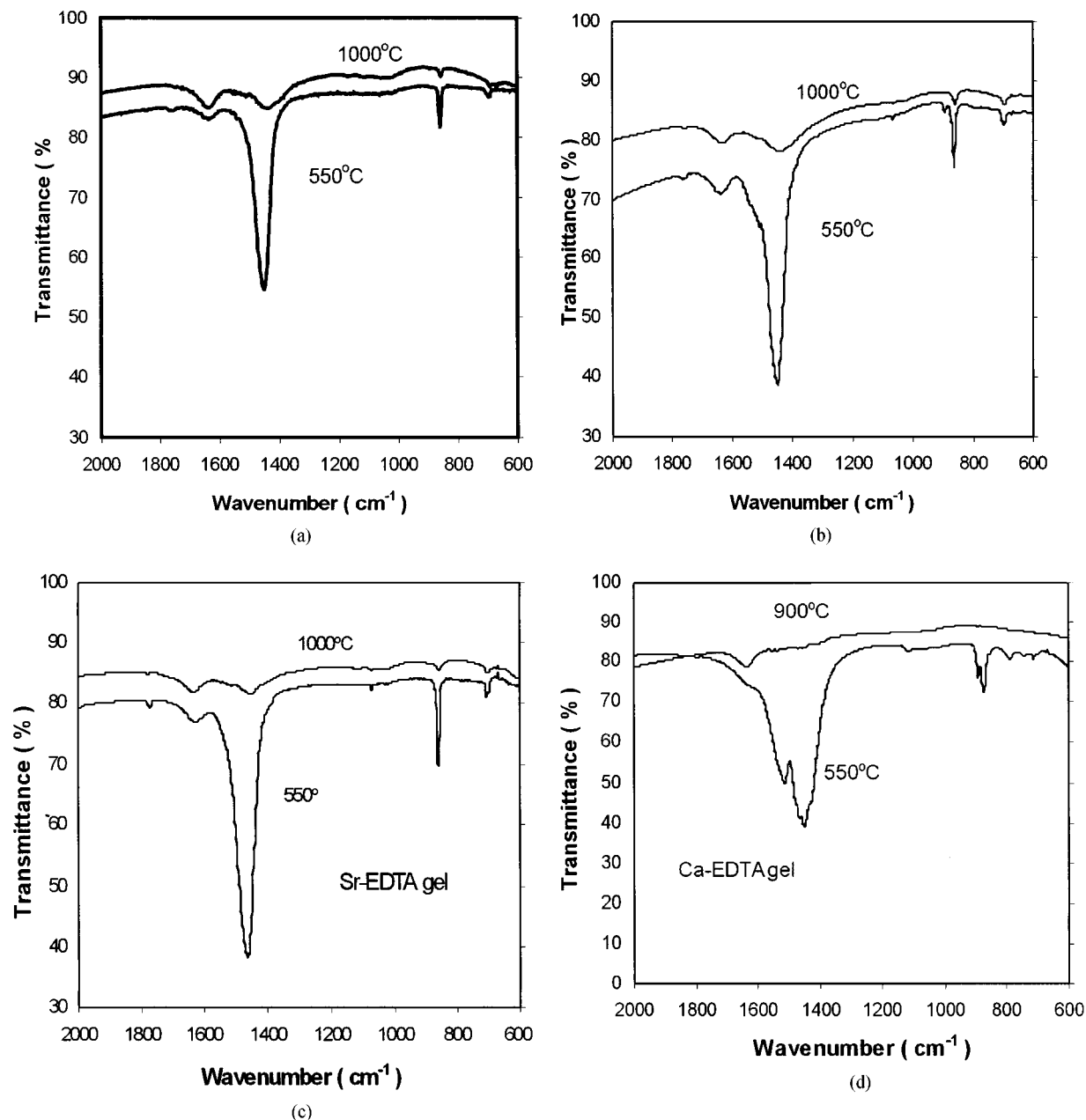


Figure 7 FTIR of the powders derived from calcination of various gel compositions at temperatures above the breakdown temperature (300°C) and the decomposition temperature (800–1000°C). (a) Ba_{0.5}Sr_{0.5}-EDTA gel; (b) Ba_{0.5}Sr_{0.45}Ca_{0.05}-EDTA gel; (c) Sr-EDTA gel; (d) Ca-EDTA gel.

3.2.1. Stage 1 decomposition

At temperatures in the range 50–200°C, the DSC (Fig. 3) and TGA (Fig. 4) analyses indicated a broad endothermic event occurred with a typical corresponding weight loss of 5–10%. This can be attributed to the loss of free and bound water from the gels.

3.2.2. Stage 2 decomposition

At slightly higher temperatures, in the range 200–425°C a second stage in the decomposition of the gels takes place. This was characterised by a small endothermic peak at around 240°C, in the DSC analysis, followed by up to three broad exothermic events at temperatures in the range approximately 250–425°C. The first event was accompanied by a corresponding substantial weight loss observed in the TGA results, with a more gradual weight loss over the range approximately

250–425°C. Such behaviour is in accordance with the findings of previous thermoanalytical studies of alkaline earth containing EDTA gels [7, 8], with the endothermic peak being associated with volatilisation of the NH₄NO₃ phase present in the gel, with the exothermic events corresponding to the initial break-down of the metal-EDTA complexes and liberation of H₂O, CO₂ and NO₂.

FTIR and XRD results obtained from the gels after heat treatment at 300°C are shown in Figs 5 and 6 respectively. These results indicate that the products resulting from this second stage of the gel decomposition comprise alkaline earth carbonates with minor impurities of the nitrate and hydroxide forms. These compounds are most probably formed by reaction of the evolved CO₂ from gel decomposition with the metal ions. In Fig. 5 the bands at 690, 860, 1455 cm⁻¹ regions can be assigned to the characteristic frequencies

of the carbonate $-\text{CO}_3^-$ groups in the alkaline earth carbonates [16], whilst the band at 1635 cm^{-1} region can largely be attributed to the hygroscopic nature of the KBr used in the sample preparation. The XRD results in Fig. 6 show that after heat treatment of the gels at 300°C , the resultant material essentially consists of the alkaline earth carbonate [20–22], with additional traces of the alkaline earth nitrate [17, 23, 24] and hydrated alkaline earth oxides [25–27]. These results also indicate that

the product obtained from the multicomponent alkaline earth gels comprised homogenous carbonate solid solutions of barium and strontium or barium, strontium and calcium according to Vegard's law [28].

3.2.3. Stage 3 and 4 decomposition

Heat treatment of the EDTA gels at temperatures above 400°C results in either one or two additional

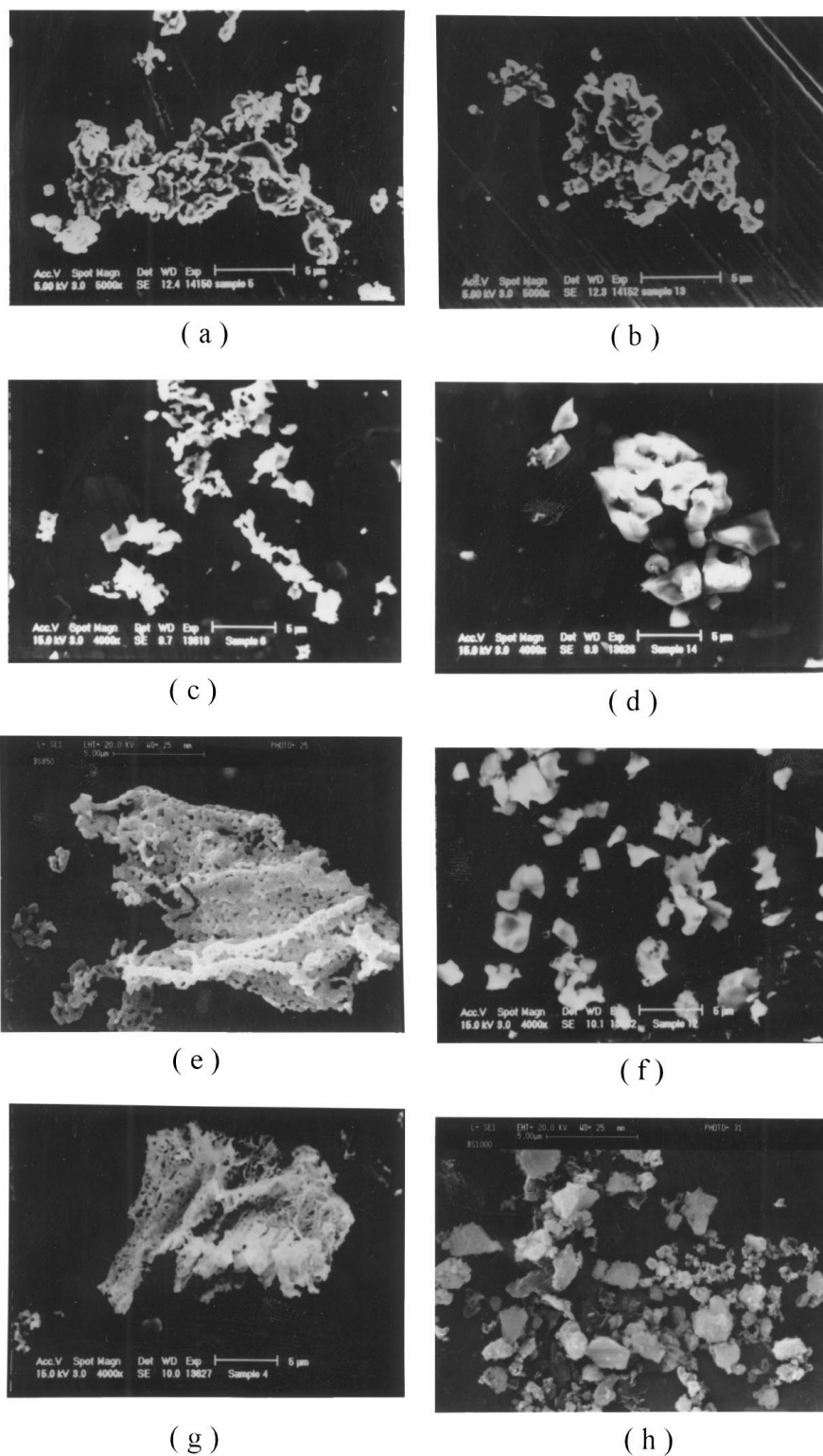


Figure 8 Morphologies of the powders derived from calcination of different gels at various temperatures. (a) Ba-EDTA, 700°C ; (b) Ba-EDTA, 850°C ; (c) Sr-EDTA, 700°C ; (d) Sr-EDTA, 850°C ; (e) $[\text{Ba}_{0.5}\text{Sr}_{0.5}]$ -EDTA, 850°C ; (f) $[\text{Ba}_{0.5}\text{Sr}_{0.5}]$ -EDTA, 1000°C ; (g) $[\text{Ba}_{0.5}\text{Sr}_{0.45}\text{Ca}_{0.05}]$ -EDTA, 700°C ; (h) $[\text{Ba}_{0.5}\text{Sr}_{0.45}\text{Ca}_{0.05}]$ -EDTA, 1000°C .

decomposition reactions according to the composition and temperature used.

DSC data, shown in Fig. 3 for the decomposition of Ba-EDTA, Sr-EDTA, Ca-EDTA and $[\text{Ba}_{0.5}\text{Sr}_{0.5}]$ -EDTA gels for temperatures up to 600 °C show a large exothermic event peaking at between 470 and 590 °C depending on gel composition, with the TGA results in Fig. 4 indicating a corresponding mass loss of around 20% for all compositions. It is believed that this decomposition stage comprises the oxidation of the residual organic material in the gel, with this event being largely eliminated when the thermal analysis was carried out under a protective atmosphere.

The results of the TGA experiments carried out at temperatures in the range 680–1000 °C indicate the occurrence of a fourth stage of decomposition in this temperature range for the materials derived from the Ca-EDTA, Sr-EDTA and BaSr-EDTA gel compositions, whilst in the case of the material derived from Ba-EDTA gel composition this event was not observed at temperatures up to 1000 °C. The corresponding mass losses were of the order of 8% for the Ca-EDTA and Sr-EDTA gel compositions and around 4% for the material derived for gel of composition $[\text{Ba}_{0.5}\text{Sr}_{0.5}]$ -EDTA.

FTIR studies of the resultant material after heat treatment at temperatures above the “decomposition temperature” for the respective compositions identified by thermal analysis showed a significant chemical change associated with this process. The results, shown in Figs 7a–d for various gel compositions indicate that this process comprises decomposition of the alkaline carbonate, which was mainly formed during the second stage. Significant differences in the thermal stabilities of the various complexes were observed in accordance with the thermal analysis results, with decomposition of the solid solution of barium and strontium carbonate, and strontium carbonate being completed after heating to 1000 °C, the decomposition of the calcium carbonate being completed after heating to 900 °C, whilst no decomposition was detected for the barium carbonate for temperatures up to 1000 °C.

Attempts to confirm the structure of the resultant oxides by XRD were of limited success due to the rapid formation of carbonate and hydroxide phases on the surfaces of the highly active particles after atmospheric exposure at ambient temperatures, both in transit to and within the diffractometer during the analysis. The structure was confirmed for CaO, which is the most stable of these oxides towards these reactions, but the surface layers of the more reactive Ba, Sr and Ba-Sr oxide particles underwent this reaction too rapidly to obtain reliable x-ray data for these compounds.

3.3. Powder characterisation

The morphologies of powders derived from calcination of Ba-EDTA, Sr-EDTA, $[\text{Ba}_{0.5}\text{Sr}_{0.5}]$ -EDTA and $[\text{Ba}_{0.5}\text{Sr}_{0.45}\text{Ca}_{0.05}]$ -EDTA gels at different temperatures are shown in Fig. 8., with the effect of composition and calcination temperature on the particle size of these powders shown in Fig. 9. Generally, powders

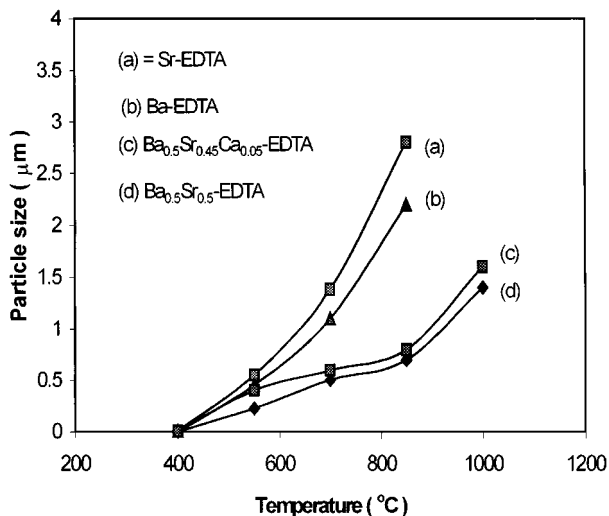


Figure 9 Effect of heat treatment temperature on the particle size of the products obtained from decomposition of alkaline earth-EDTA gels.

with fine particle size were obtained at relatively low temperatures with the particle size increasing with increasing calcination temperature above approximately 500 °C. In addition, a relation between the particle size and the composition of the powders was observed, with the powders from the multicomponent $[\text{Ba}_{0.5}\text{Sr}_{0.5}]$ -EDTA gel and $[\text{Ba}_{0.5}\text{Sr}_{0.45}\text{Ca}_{0.05}]$ -EDTA gels forming finer particles at equivalent decomposition temperatures throughout all stages of the decomposition than those obtained from either barium-EDTA or strontium-EDTA gels. This finding is consistent with similar results obtained from studies of the decomposition of conventionally prepared alkaline earth carbonates [29, 30].

The morphology of the gel derived materials generally comprised larger agglomerates of submicron sized particles. The primary particles formed were initially rounded in shape, increasing in size significantly and changing to a more angular morphology on heat treatment above the carbonate decomposition temperature. The effect, on the particle morphology, of heating to temperatures above the carbonate decomposition temperature can be seen by comparing the respective pairs of micrographs shown in Fig. 8c and d; 8e and f; 8g and h.

4. Conclusions

The EDTA-gel process has been successfully used for the production of a homogeneous gel of single and multicomponent alkaline earth-EDTA compositions, with control of the pH value at an appropriate level being identified as a key parameter in the process.

Subsequent thermal decomposition of these gels has been shown to result in the formation of single or multicomponent carbonate solid solutions at temperatures below 300 °C, with the corresponding oxides being formed after heat treatment at higher temperatures.

The powders resulting from this process are chemically homogenous, with fine particle size, and compare favourably with powders prepared by conventional precipitation techniques.

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