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Technological studies

In celebration of the 60th birthday of Dr. Andrew K. Galwey

A THERMOANALYTICAL STUDY OF THE METAL NITRATE-EDTA PRECURSORS FOR LEAD ZIRCONATE TITANATE CERAMIC POWDERS

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Abstract

Lead zirconate titanate (PZT) ceramic powder has been synthesized from metal nitrate solutions using the EDTA-gel method with different nitric acid/EDTA ratios. It was found that the thermal decomposition of the precursor was strongly affected by the nitric acid/EDTA ratio, the amount of sample, the atmosphere, and the heating rate. Crystallization of the perovskite PZT phase initiated at external temperatures as low as 250°C, as a result of the exothermic decomposition reaction of the nitrate-EDTA complexes. Possible reaction schemes are suggested and discussed to describe the thermal decomposition of PZT-EDTA precursors under different experimental conditions.

Keywords: ceramics

Introduction

The thermal decomposition of amorphous precursors prepared by the citrate process has been studied by several authors [1–3]. Courty *et al.* [1] suggested that the oxidation/decomposition of the citrate-nitrate complexes produced during processing may be explained by a simplified reaction involving citric acid and nitrate ions, as follows:

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$$6NO_3^- + C_6H_8O_7 \rightarrow 6CO_2\uparrow + H_2O\uparrow + 6OH^- + 6NO\uparrow \qquad (1)$$

Both the reactants involved have been used on their own for the production of powders. It is interesting to note that with metal nitrates alone, there may be problems of melting prior to decomposition which gives chemical segregation. With pure citrates the oxidation/decomposition reactions are not easily achieved. However, when both are present, as effectively occurs in the solid citrate-nitrate complex precursors, the solid matrix is preserved and prevents segregation, and an open porosity is developed within the precursor. The organic part of the precursor is more easily oxidized, because of the open porosity and the presence of the nitrate ions as an 'in-situ' oxidizing agent. Sale *et al.* [3–5] have confirmed that, using mass spectrometry, the evolved gas products on decomposition/oxidation are CO_2, H_2O and NO.

Two types of pyrolysis of the precursors were recognized by Courty [1]. Type I corresponds to precursors containing nitrate ions and metals (Fe, Ni, Ag, Cu, Co) having a strong catalytic activity in oxidation. The corresponding thermogravimetric curve usually shows a continuous and energetic single-step reaction. Type II is characterized by an intermediary decomposition step to a semi-decomposed substance which is typically thought to be a mixed citrate salt. In this case, thermogravimetry shows a two-step profile. Ideally, pyrolysis of type I is preferred, since there is less opportunity for compositional segregation.

Ethylene-diamine-tetra-acetic acid (EDTA) is widely used in analytical chemistry as a complexing agent and has recently been used in the production of superconductor ceramic powders [6–8] via gels, due to its strong complexing ability with most metal ions. The structural formula of EDTA and the typical geometry of the EDTA chelated complex are shown in Fig. 1. Although the complexing behaviour and structural configurations are well studied [9–10], knowledge of their decomposition behaviour is limited. In the studies of superconductor production by the EDTA-gel route, type II pyrolysis behaviour was observed [6–8]. The first major mass loss from 200–250 °C was identified as the breakup of the EDTA compounds and the dissociation of NH_4NO_3, while the last mass loss is thought to be associated with the final decomposition and oxidation to give the oxide [6]. In a previous study [11], amorphous precursors were prepared via the EDTA-gel route for the production of lead zirconate titanate (PZT) powders. A more complete decomposition of the precursor was observed when the starting solutions contained a higher nitric acid/EDTA ratio. Also, the decomposition behaviour of the PZT-EDTA precursor was found to be dependent on the heating conditions. The main objective of the present work is to clarify how, in addition to the catalytic effect of the metallic elements, the ex-

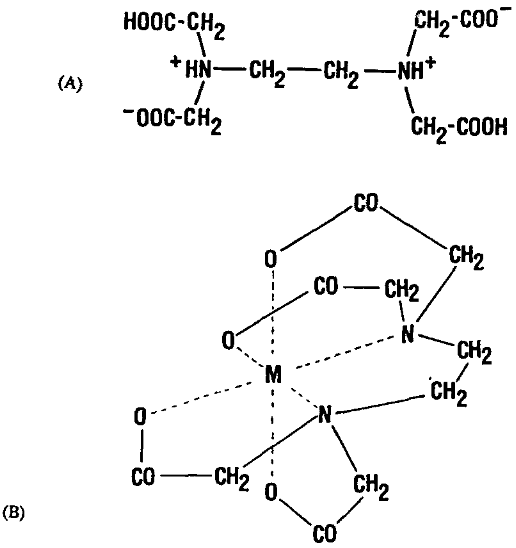

Fig. 1 (a) Structural formula of EDTA and (b) typical geometry of the EDTA chelated complex

perimental variables and nitric acid/EDTA ratio may affect the decomposition behaviour of the metal-EDTA gel, since these might exert a strong influence on the morphology and sinterability of the resulting powder.

Experimental

The detailed preparation of the PZT-EDTA precursors has been described [11]. The composition chosen for investigation was $Pb_{1.1}(Zr_{0.52}Ti_{0.48})O_3$. The metal nitrate solutions were mixed in stoichiometric proportions and then gradually added to the EDTA solution while the *pH* was maintained at 5 by the

Table 1 Compositions of EDTA-chelated precursors

Identifier	PZT	EDTA	NH_3	NO_3	NO3/EDTA	Volatile/
		(mole)			ratio	wt%*
PZT1	0.1	0.15	1.27	0.62	4.13	75.0
PZT2	0.1	0.15	1.67	0.81	5.40	78.0

PZT = $Pb_{1.1}(Zr_{0.52}Ti_{0.48})O_3$, M.W. = 346.337 g·mol^{-1}

EDTA: M.W. = 292.24 g·mol^{-1}

NH_3 solution: 35%, density = 0.88 g/cm^3

HNO_3 solution: 70%, density = 1.42 g/cm^3

*Calculated assuming that all the H_2O from the nitrates (and only the H_2O) is removed during vacuum drying.

addition of ammonia solution. The liquid was dried in a vacuum at 80°C to produce the desired precursors. Solutions were prepared having different values of the nitrate/EDTA ratio, as shown in Table 1 together with theoretical calculations of the volatile content of these precursors.

The decomposition behaviour was characterised by simultaneous thermal analysis (DTA/TG/DTG) carried out from room temperature to 1000°C using a Seiko SSC/5200 system. In order to clarify the influence of the experimental variables on the decomposition characteristics, tests were carried out with a number of different sample sizes (1, 3, 5 and 10 mg) and heating rates (1, 2, 5, 10, 20, 30, 40 deg·min^{-1}), and in various atmospheres (argon, nitrogen, air and pure oxygen). The evolved gas products were analyzed using a mass spectrometer in an air atmosphere. The resulting phases and powder morphologies of the precursors after calcination were examined using XRD and SEM. During all experiments, platinum crucibles of dimensions 5 mm o.d, 2.5 mm ht. were used. In the Seiko system, sample temperature measurement is obtained by a thermocouple which is positioned beneath the specimen crucible on the balance arm.

Results

Thermal decomposition behaviour

The effect of nitric acid/EDTA ratio.

Figure 2 shows the typical DTA/TG curves obtained for the decomposition of the PZT1 and PZT2 gels in air, with a sample mass of 10 mg and a heating rate of 10 deg·min^{-1}. Both PZT-EDTA gels show one or two small endothermic peaks around a temperature of 200°C and almost complete decomposition after two sharp and large exothermic reactions at 210–240°C. The total mass losses agree well with the values calculated assuming complete loss of all the volatile components (75.5% for the PZT1 gel and 78.5% for the PZT2 gel at 700°C). For the PZT2 gel, a more complete decomposition and loss of volatile material was observed after the exothermic reaction at 240°C. The effect of excess nitric acid on the thermal decomposition of the organic component is clear in the case of the PZT2 gel, which exhibited a much sharper exotherm and a mass loss which was virtually complete at an external temperature of 250°C.

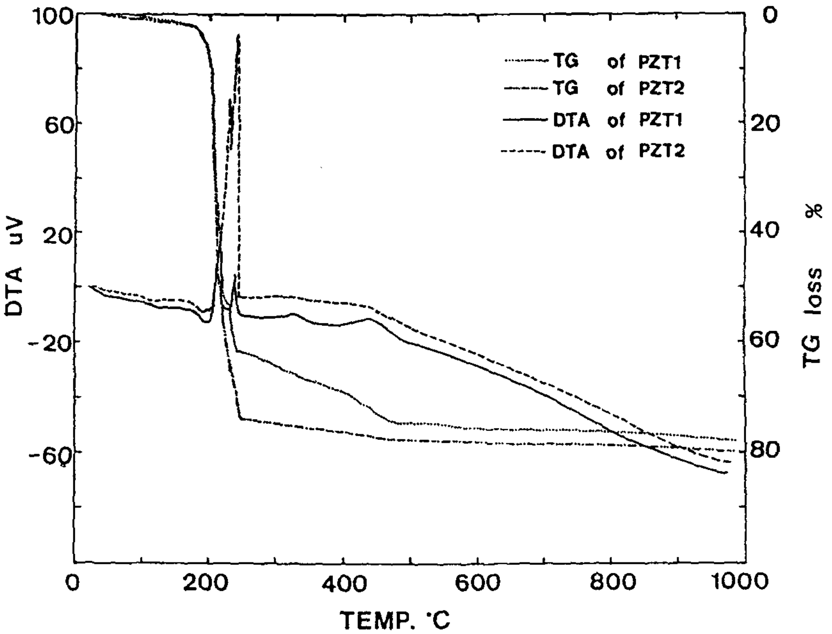

Fig. 2 DTA/TG curves for PZT1 and PZT2 precursors. The total mass losses agree with those calculated on the basis of the amount of volatile material present

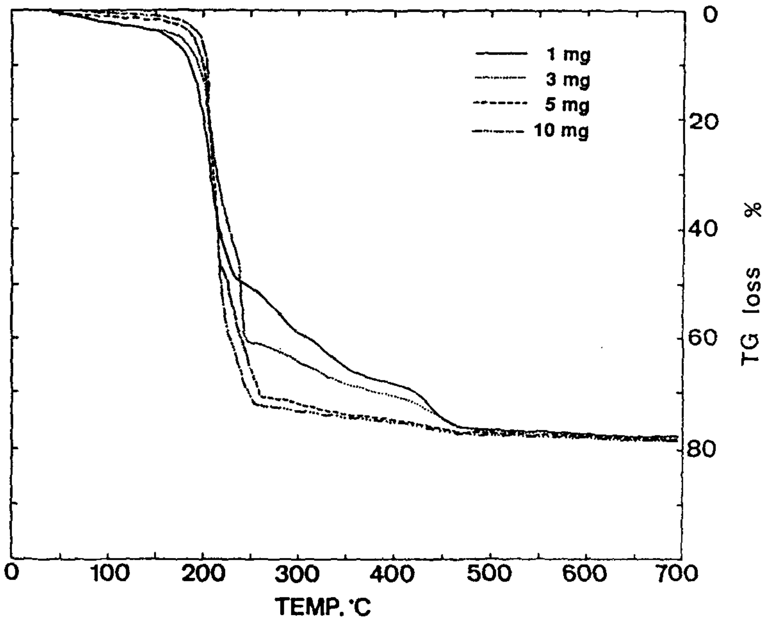

Fig. 3 The effect of sample size on decomposition of the PZT2 precursor, as measured by TG

The effect of sample size

Thermogravimetric data showing the decomposition of the PZT2 gel as a function of the sample size, with a heating rate of 10 deg·min^{-1} in air, are given in Fig. 3. It is clear that a more complete decomposition was observed for the larger sample sizes. This is attributed to the greater self-heating of these samples at temperatures from 210 to 240°C, which increased the internal temperature of the sample by an estimated 40°C.

The effect of atmosphere

Figure 4 shows the thermal analyses of the PZT2 gel (for a 10 mg sample) carried out in argon and pure oxygen, in order to allow a comparison with the results previously obtained in air. The results obtained in nitrogen were almost identical to those obtained in argon, and will not be shown here. It was found that the fractional mass losses occurring after the main exothermic reaction, at temperatures between 250 and 700°C, were 11.0% in argon (10.5% in nitrogen), 7% in air, and 2.6% in pure oxygen, i.e. a more complete low temperature decomposition/oxidation occurs in oxygen than in air or argon. These results suggest that, in addition to the presence of excess nitric acid or nitrate ions as

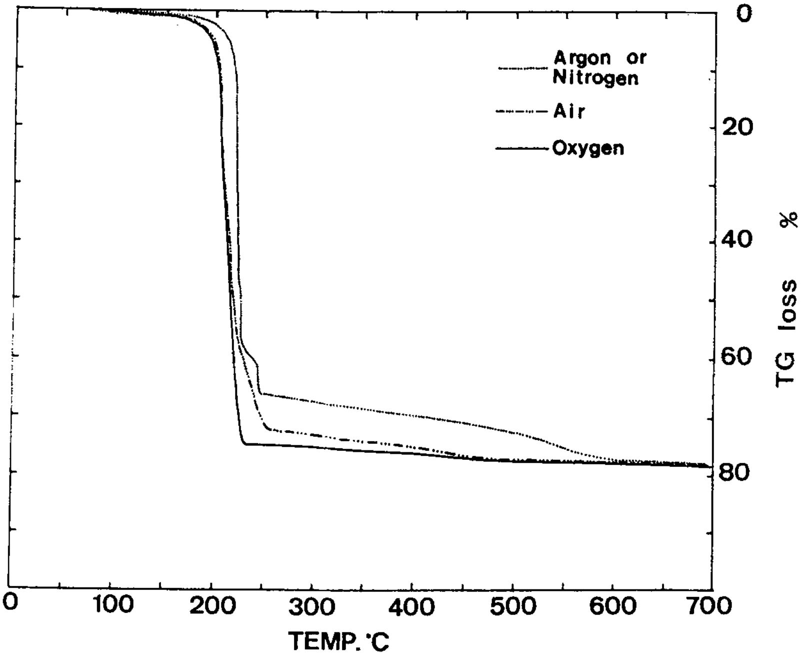

Fig. 4 The effect of atmosphere on the decomposition of the PZT2 precursor

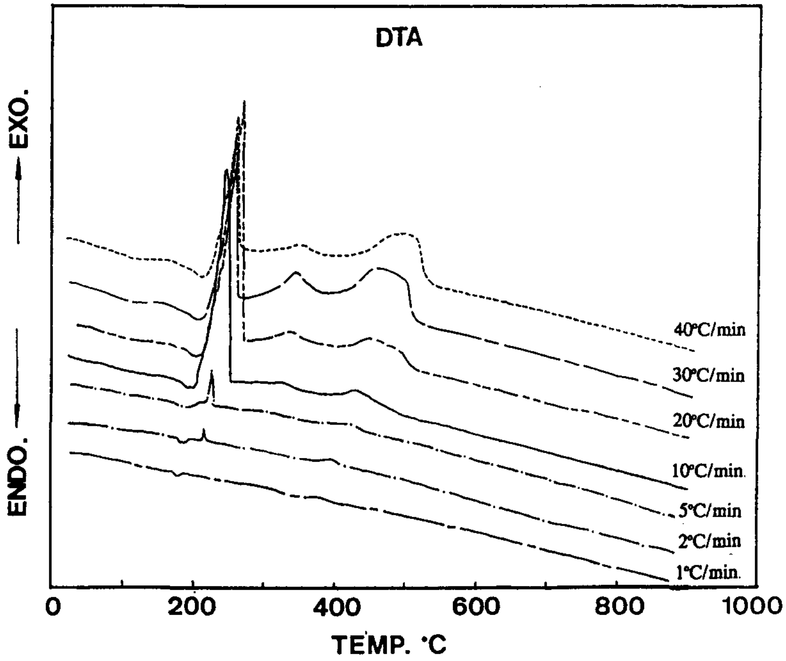

Fig. 5(a) DTA curves for PZT2 precursor at heating rates from 1–40 deg·min^{-1}

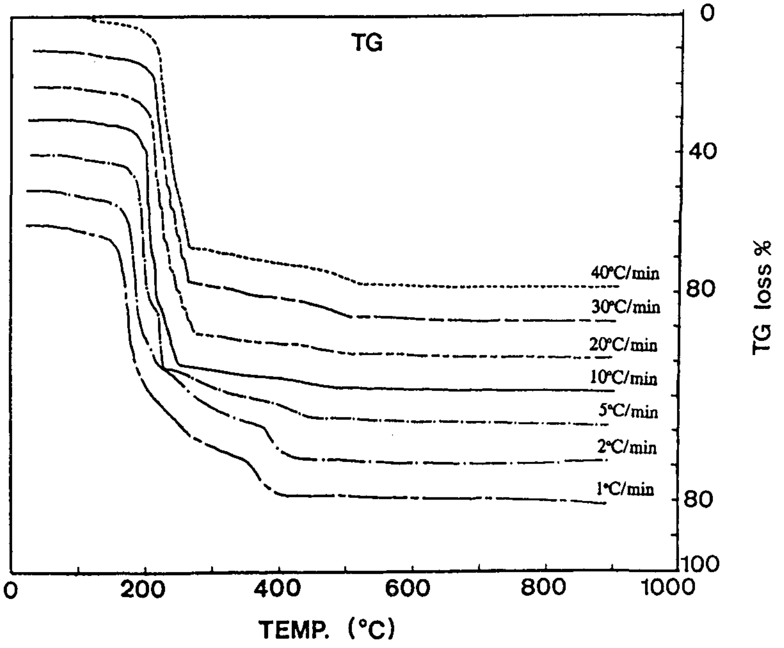

Fig. 5(b) TG curves for PZT2 precursor at heating rates from 1–40 deg·min^{-1}

an 'in-situ' oxidant, oxygen in the atmosphere also plays a significant role during the decomposition/oxidation of the PZT-EDTA gel. Therefore, any simplified reaction used to describe the decomposition/oxidation of the EDTA-nitrate gel precursor must involve oxygen, nitrate ions and EDTA.

The effect of heating rate

The DTA/TG/DTG results obtained for 8 mg samples of the PZT2 gel (in air) at heating rates from 1 to 40 deg·min^{-1} are shown in Fig. 5(a), Fig. 5(b), and Fig. 5(c), respectively. At the lowest heating rate (1 deg·min^{-1}), only one small endothermic peak and one small exothermic peak are evident, at 185 and 374°C, respectively. These two peaks were shifted to temperatures of 190 and 392°C with a heating rate of 2 deg·min^{-1} and a small, sharp exothermic peak is apparent at 216°C which was accompanied by a mass loss of ≈ 6%. The DTG results (Fig. 5(c)) indicate that this may be a separate reaction. For a heating rate of 5 deg·min^{-1}, this separate reaction was more intense, causing a sharper and larger mass loss (~17.5%) and larger exothermic peak. However, the separate reactions occurring at temperatures below 250°C were not apparent for

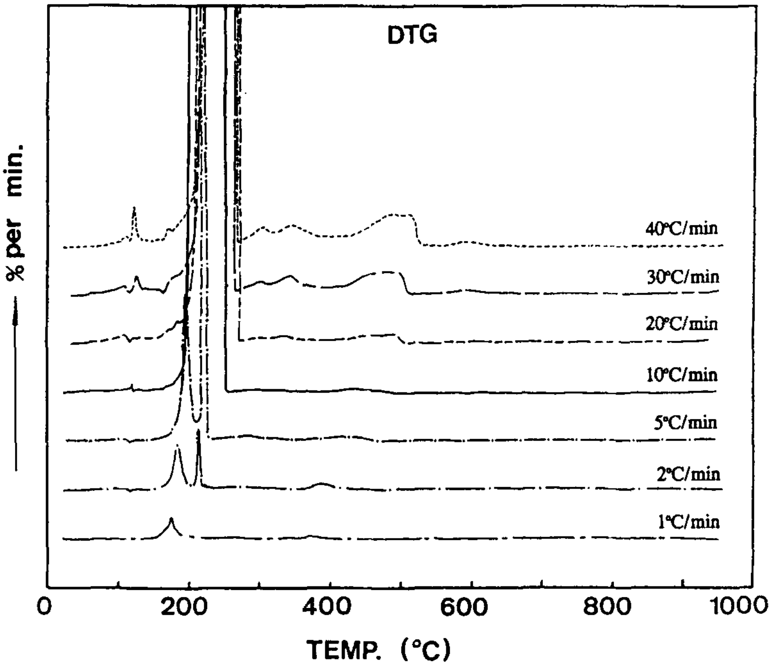

Fig. 5(c) DTG curves for PZT2 precursor at heating rates from 1–40 deg·min^{-1}

heating rates greater than 10 deg·min^{-1} and seemed to appear as a large exothermic reaction extending over the temperature range from 210 to 270°C. The exothermic peak height and internal temperature in the powder sample in this temperature range were dependent on the amount of sample. The residual mass losses on heating from 250 to 700°C were measured as $\approx$ 7% for heating rates of 10 and 20 deg·min^{-1} and $\approx$ 12% for heating rates of 30 and 40 deg·min^{-1} (Fig. 5(b)). For the latter cases, these residual materials caused further broad oxidative exothermic reactions at higher temperatures (330–500°C in Fig. 5(a)). This variation in the residual mass loss after the initial reaction may be explained if the amount of in-situ oxidant able to react with the EDTA is dependent on the heating rate, as will be discussed below. Table 2 shows the mass losses recorded at different heating rates after the large exothermic reaction at 220–270°C, and the final mass losses obtained at 700°C. Clearly, there is an optimum heating rate of 10–20 deg·min^{-1} to achieve the minimum organic reaction residue within the oxide product after the main exothermic decomposition reaction. It is clear that subsequent heating to 700°C removes the residual carbonaceous materials from the powder samples. However, this may result in particle enlargement and so the time spent at the upper temperature should be minimized, i.e. the lower residual content after the main reaction at 210–270 °C is required.

Table 2 Mass loss of PZT2 precursor under different heating rates

Heating rate/ deg·min^{-1}	Exothermic reaction A	Final mass loss /% B	Difference A–B
1	201°C, –46.0	700°C, –78.6	32.6
2	224°C, –50.9	700°C, –78.0	27.1
5	235°C, –61.6	700°C, –77.5	15.9
10	257°C, –71.0	700°C, –78.0	7.0
20	275°C, –71.4	700°C, –78.5	7.1
30	271°C, –66.4	700°C, –78.0	11.6
40	271°C, –66.3	700°C, –78.0	11.7

Evolved gas analysis (EGA)

The EGA data indicated that the gaseous products were NH_3, H_2O, NO and CO_2. Figures 6(a),(b) show the gases evolved during thermal decomposition for the PZT2 gel. The precursors were heated from room temperature to 500°C at heating rates of 10 deg·min^{-1}. (Fig. 6(a)) and 2 deg·min^{-1}. (Fig. 6(b)) under flowing air (20 ml/min). For the heating rate of 10 deg·min^{-1}, the four gaseous products were evolved from 190 to 240°C and peaks were sharp and located around 210°C. When the heating rate was 2 deg·min^{-1}, the signals associated with these gaseous products decreased significantly as a result of a lower product concentration obtained at any given point in time because of dilution effects of the dynamic gas atmosphere in the furnace. In addition, all the peaks became broad and shifted to lower temperatures thus indicating reactions over a wider range of temperatures. In particular, the amount of CO_2 was diminished rather more than expected as a result of the change in heating rate and indicates that the exothermic reaction, which is important for the decomposition/oxidation of the EDTA, only becomes intensive at a heating rate of 10 deg·min^{-1} and above. The gaseous products from the nitrate-EDTA, precursors are similar to those observed in the decomposition of amorphous citrate gels, suggesting that a similar reaction scheme may be involved.

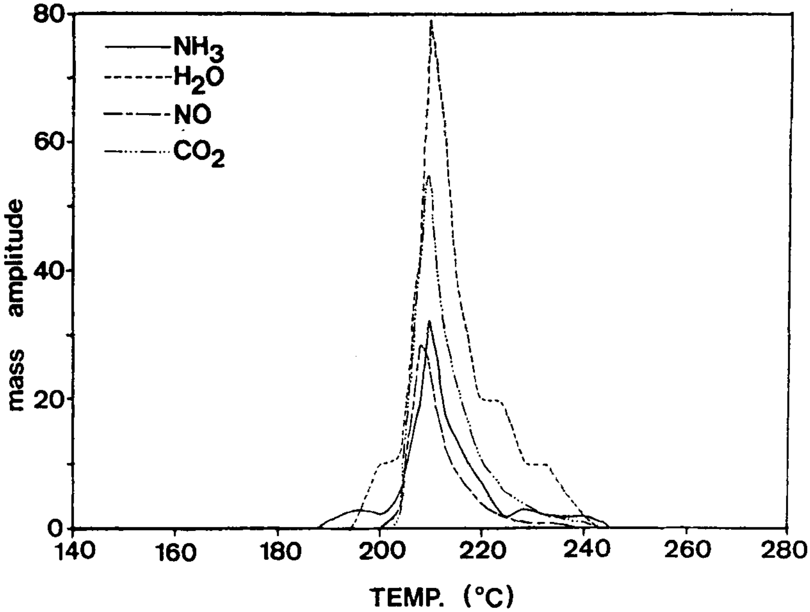

Fig. 6(a) Evolved gas analysis by mass spectrometry for the PZT2 precursor at a heating rate of 10 deg·min^{-1}

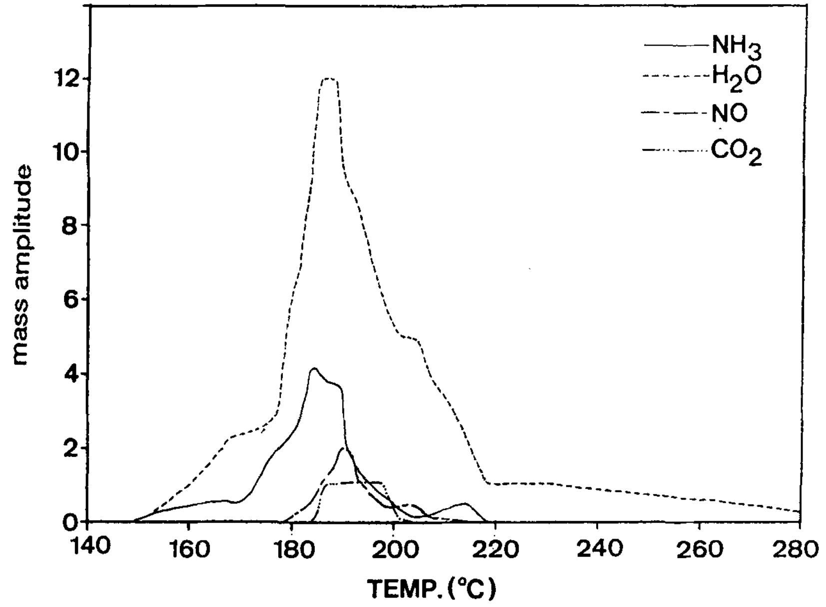

Fig. 6(b) Evolved gas analysis by mass spectrometry for the PZT2 precursor at a heating rate of 2 deg·min^{-1}

Oxide phase development

XRD data, giving the sequence of crystalline phases formed during the course of thermal treatment of the PZT2 precursor, are shown in Fig. 7 (results for the PZT1 precursor were similar). It is apparent that the as-dried gel was amorphous, but contained some crystalline ammonium nitrate (NH_4NO_3) as a minor phase. The ammonium nitrate was produced by reaction between the ammonia, used for pH control, and free nitric acid and decomposed to yield gaseous NH_3 when heated to 200°C. The gaseous ammonia product was confirmed by mass spectrometry at a temperature of 190–210°C. Thus, it is clear that the endothermic peak at 200°C in the DTA curve (Fig. 2) is caused by the decomposition of the ammonium nitrate. Further decomposition and oxidation of the organic of the organic part evolves a considerable amount of heat which increases the local temperature in the precursor and causes burning of the residual carbon. The nitrate ions provide an oxidising environment for the PZT-EDTA complexes and thus facilitate the decomposition and oxidation of the precursor. A pure PZT phase, together with some PbO, was readily formed after calcination at only 250°C. The XRD peaks corresponding to PZT became more clear and sharp at higher temperatures, and no intermediate $PbTiO_3$ phase was observed.

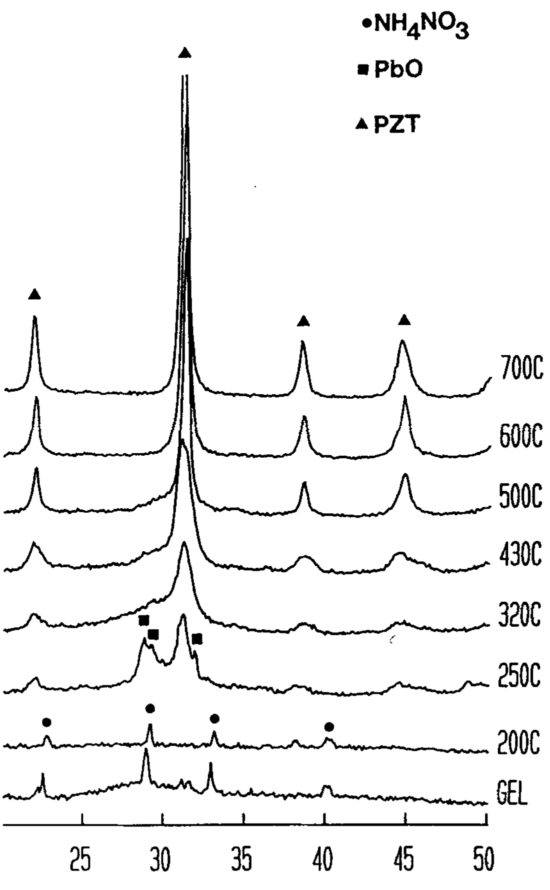

Fig. 7 Phase development of the PZT2 precursor after calcination for 1 hr at various temperatures

The PZT-EDTA precursor produced a porous and friable powder after calcination at temperatures greater than 250°C. This porous material sintered into large crystalline agglomerates after subsequent calcination at higher temperatures. A fine, homogeneous and pure PZT ceramic powder, with a mean particle size ≈ 0.1–0.3 μm, could be produced using a heating rate of 10 deg·min^{-1}. The powders produced using either a slow heating rate, or an extremely fast one, exhibit strong agglomeration.

Discussion

From the results given above, it is clear that increasing the nitric acid/EDTA ratio, the sample size, the heating rate, and the use of an oxygen atmosphere, all increase the extent of thermal decomposition of the PZT-EDTA gel. The decomposition reaction given above (Eq. (1)) to represent the reaction which occurs in the presence of free nitrate ions in a citrate gel suggests complete oxidation of the organic component without any residual carbon. However, from previous work on citrate gels [3], it has been found that there is always a considerable amount of residual carbon left in the powder if the calcination temperature is lower than 1000°C. If the stoichiometry of the suggested reaction is maintained, then this residual carbon should not be observed. If the decomposition were to be carried out in an oxygen-deficient atmosphere, or conditions where the stoichiometry of reaction (1) does not apply, the carbon of the organic component would not necessarily be converted completely to carbon dioxide. The kinetically-preferred reaction at low temperature in an oxygen-deficient atmosphere may be represented by:

$$2NO_3^- + C_6H_8O_7 \rightarrow 3C + 3CO_2\uparrow + 3H_2O\uparrow + 2OH^- + 2NO\uparrow \qquad (2)$$

which involves only two reactant molecules. However, in an oxygen-containing atmosphere, Eq. (3) may more correctly represent the reaction that occurs:

$$2NO_3^- + C_6H_8O_7 + 3O_2 \rightarrow 6CO_2\uparrow + 3H_2O\uparrow + 2OH^- + 2NO\uparrow \qquad (3)$$

In such a way, it would be theoretically possible to oxidize all of the carbon present in the citrate gel. However, if the gel were to be decomposed in an inert atmosphere and the stoichiometry of Eq. (1) was not present, there would always be some residual carbon as indicated in Eq. (2).

From this argument, it is possible to devise a series of the possible reactions between nitrate ions and EDTA in the precursor at various stoichiometries during heating in an inert atmosphere. Such reactions may be expressed generally, as given in Eq. (4). CO is not included in the reaction products at these temperatures as CO_2 is the thermodynamically most stable oxide of carbon at temperatures up to 500°C under standard conditions.

$$xNO_3^- + yC_{10}H_{16}N_2O_8 \rightarrow zC + aCO_2 + bH_2O + cOH^- + dNO \qquad (4)$$

Kinetically, it may be suggested that the following reactions should be preferred on the basis of the smallest number of reacting molecules:

$$4NO_3^- + 2C_{10}H_{16}N_2O_8 \rightarrow 19C + CO_2\uparrow + 14H_2O\uparrow + 4OH^- + 8NO\uparrow \qquad (5)$$

$$4NO_3^- + C_{10}H_{16}N_2O_8 \rightarrow 8C + 2CO_2\uparrow + 6H_2O\uparrow + 4OH^- + 6NO\uparrow \qquad (6)$$

It is clear that for decomposition in the inert atmosphere, the presence of excess nitric acid in the gel should give products containing less residual carbon, and more carbon dioxide should be formed, relative to situations where less nitric acid is present. However, if sufficient oxygen is available from the gas phase, the reaction represented by Eq. (5) may be modified as follows:

$$4NO_3^- + 2C_{10}H_{16}N_2O_8 + 19O_2 \rightarrow 20CO_2\uparrow + 14H_2O\uparrow + 4OH^- + 8NO\uparrow \quad (7)$$

If the supply of oxygen is limited, the reaction would not be as complete as that given in Eq. (7). Less oxygen will participate in the reaction and some residual carbon will be present. The effect of oxygen on the decomposition/oxidation of the gel was demonstrated by the results given for the PZT2-EDTA gel (Fig. 4). The masses of residual organic material present after heating to 250°C in nitrogen or argon were 10.5 to 11%. According to Eq. (5), for decomposition in an inert atmosphere, ≈ 39% of the EDTA organic would be left after the reaction. Applying this prediction to the PZT2 gel, which also contains metal ions, the predicted mass loss is 10.8% of the total precursor mass, which is in excellent agreement with the experimental results. The lower amount of residual material, present after the large exotherm for gels decomposed in air and pure oxygen, is due to a more complete oxidation reaction, as indicated in Eq. (7).

In this study, the molar ratios of nitric acid to EDTA were 4.13 and 5.40 for the PZT1 and PZT2 gels respectively. Therefore, in the inert atmospheres it might be expected that the reaction represented by Eq. (6) would be preferred to that given in (5). However, if the nitric acid/nitrate ions were to begin to decompose to produce the in-situ oxidants at temperatures lower than that at which the organic component decomposed, the effective ratio of nitric acid to EDTA would not be 4 at the time of the gel oxidation/decomposition reaction. Also, the rate of heating would determine the level of 'in/situ' oxidant available to participate in the organic oxidation/decomposition reaction. It seems that this situation exists for the decomposition carried out in inert atmospheres, as shown in Fig. 4. The use of slower heating rates gave rise to the well-separated exothermic reactions at temperatures between 210 and 240°C and allowed the loss of some nitrate as gaseous oxides, thus leaving a greater proportion of residual carbon (Fig. 5(a)–(c)). For the medium heating rates, such as 10 and 20 deg·min^{-1} minute in air, the stoichiometry of reaction (6) occurred, as little time was available for the diffusion of the oxidising agents away from the reaction site. Hence, the experimental data agree well with the predicted data. It is understandable that the slightly lower residual carbon content found experimentally after firing in air is due to the partial oxidation of carbon. With more rapid heating rates, such as 30–40 deg·min^{-1}, more residual material was left. To explain this, we have to reconsider the effect of heating rate on the generation of the in-situ oxidants and on the decomposition of the EDTA complexes.

The suggested reaction (6) is a simplified reaction between nitrate ions and EDTA. In fact, it is the decomposition of NH_4NO_3 that should be considered within the gels produced in this study, since this is a major source of nitrate ions or oxidising gases at low temperature. The decomposition of NH_4NO_3 may be expressed as:

$$2NH_4NO_3 \rightleftarrows 2NH_3 + H_2O + 2NO_2 + \tfrac{1}{2}O_2 \qquad (8)$$

Under ideal circumstances the oxidizing agents need to be present at the time when the EDTA complexes break to give complete decomposition/oxidation. If the heating rate is so slow that the oxidizing species have diffused from the reaction site by the time that the temperature has reached 220–240°C, where the EDTA complex starts to break, then complete decomposition/oxidation does not occur. On the other hand, if the heating rate is so fast that the EDTA complexes decompose rapidly and time is not available for the diffusive supply of oxidizing species, then the decomposition/oxidation is again not complete. Such behaviour occurred during the fast heating such that more residual carbon was left after the exothermic reaction at 270°C.

Conclusions

The thermal decomposition of the PZT-EDTA precursor was found to be sensitive to the nitrate ions/EDTA ratio, sample size, atmosphere, and heating rate. In general, the thermal decomposition behaviour can be explained by a simplified reaction mechanism between nitrate ions and EDTA. Higher nitric acid/EDTA ratios, and a heating rate of 10–20 deg·min^{-1} produced a larger exothermic reaction during decomposition/oxidation as a result of more in-situ oxidizing agent being available to react with EDTA. More residual carbon was left at lower and higher rates because the rate of supply and quantity of oxidant available by in-situ generation was not able to match that required for complete oxidation of the decomposed organic species.

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Zusammenfassung — Unter Anwendung der EDTA-Gelmethode wurden mit verschiedenen Salpetersäure/EDTA-Quotienten aus den Metallnitratlösungen Keramikpulver aus Bleizirkonattitanat (PZT) synthetisiert. Man fand, daß die thermische Zersetzung des Präkursors stark durch den Salpetersäure/EDTA-Quotienten, durch die Probengröße, die Atmosphäre und die Aufheizgeschwindigkeit beeinflußt wird. Die Kristallisation der PZT-Phase Perowskit wurde bei so niedrigen äußeren Temperaturen wie etwa 250°C im Ergebnis der exothermen Zersetzungsreaktion des Nitrat-EDTA-Komplexes initiiert. Zur Beschreibung der thermischen Zersetzung von PZT-EDTA-Präkursoren unter verschiedenen experimentellen Bedingungen wurden mögliche Reaktionsschemen vorgeschlagen und erörtert.