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EFFECTS OF METAL SALTS ON THE THERMAL DECOMPOSITION OF EDTA-GEL PRECURSORS FOR FERROELECTRIC CERAMIC POWDERS

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Abstract

Raw chemicals such as metal nitrates and chlorides were found to affect the thermal decomposition behaviour of EDTA-gel precursors used for the production of ceramic powders. Fine, homogeneous ceramic powders were produced from nitrate solutions while chlorides gave segregated phases. In studies on the production of lead zirconate titanate (PZT) using chlorides, the segregation and loss of lead was observed and shown to be caused by the formation and evaporation of $PbCl_2$. Thermal analysis (DTA/TG) quantitatively proved the suggested reaction mechanism for this phase segregation. Crystallization of the desired perovskite phase of lead zirconate titanate (PZT) and barium titanate (BT) initiated at temperatures as low as 250°C in the nitrate-EDTA precursors. Water of crystallization and formation of $BaCO_3$ in the barium titanate precursor were suggested to account for differences in the observed decompositional behaviours of the BT and PZT precursors.

Keywords: EDTA-gel precursors, ferroelectric ceramic powders

Introduction

Ferroelectric and superconducting oxide powders may be synthesized by a variety of chelating and sol-gel methods. For the aqueous gel techniques, precursors are prepared from the corresponding metal nitrate solutions using chelating agents such as citric acid [1–3] and ethylene diamine tetraacetic acid (EDTA) [4–6]. The thermal decomposition of gel precursors prepared by the citrate process has been studied by several authors [7–9] but those of EDTA precursors were studied only recently [4–6, 10]. The organic part of the precursor is more easily oxidized, because of the initiating and oxidizing effect of nitrates [7, 8, 10]. It is known that chloride ions are not decomposed during thermal decomposition, but the details of the influences of the different anions are not well understood [11]. Furthermore, different metal elements may lead to a different decompositional behaviour [8]. Simultaneous thermal and evolved gas analysis offers a powerful technique to study these differences. This paper pre-

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sents a thermoanalytical study on the thermal decomposition of gel precursors made from different raw chemicals.

Experimental procedure

Chemicals

EDTA: Aldrich Chem. Co. Ltd. No. E26282
$Pb(NO_3)_2$: Fluka Chemika, No. 15335
$ZrCl_4$: Fluka Chemika, No. 96600
$TiCl_4$: Fluka Chemika, No. 89541
$Ba(NO_3)_2$: Fluka Chemika, No. 11787

Instruments

DTA/TG: SSC/5200, TG/DTA 320, Seiko Instrument, Aug. 1989
XRD: Philips PW 1710 powder diffractometry
EGA: INFICON Quadrex PPC mass spectrometry

The starting reagents used were high purity, analytical grade, EDTA acid (>99%), $Pb(NO_3)_2$ (>99%), $Ba(NO_3)_2$ (>99%), $ZrCl_4$ (>98%) and $TiCl_4$ (>98%). The nitrate solutions of zirconium and titanium were prepared separately by dissolving zirconium and titanium hydroxides in nitric acid. The hydroxide precipitates were previously obtained by adding $ZrCl_4(aq)$ and $TiCl_4(aq)$ to ammonia solution, followed by triple filtering and washing with deionized water to remove residual chloride ions. Highly concentrated nitric acid and a chilled environment were required to dissolve the zirconium hydroxide and titanium hydroxide precipitates [12]. The concentrations of metal ions in the nitrate solutions were determined by using a simple gravimetric technique, where a specific volume of each solution was evaporated and calcined at 1000°C for 1 h, forming their respective oxides. EDTA acid solution with $pH = 5$ was prepared by dissolving EDTA acid in deionized water and adding the minimum required amount of ammonia solution.

The ceramic compositions chosen for investigation were $Pb_{1.1}(Zr_{0.52}Ti_{0.48})O_3$ and $BaTiO_3$. The desired metal nitrate or chloride solutions were gradually added to the EDTA solution individually while the pH value was maintained at a value of 5 by the addition of ammonia solution. The resulting clear solution was evaporated under vacuum in a revolving flask at 50–70°C until a viscous liquid was obtained. No precipitation was observed during evaporation. The viscous liquid was dried in a vacuum oven at 80°C for 24 h 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 volatile materials in these precursors.

Table 1 Composition of EDTA-chelated precusor

Name	PZT/ mole	BT/ mole	EDTA/ mole	NH_3/ mole	NO_3/ mole	Cl/ mole	NO_3/EDTA ratio	volatile (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	78.1
PZTCl	0.1		0.15	1.18	0.22	0.4	1.47	72.6
BT1		0.1	0.11	1.02	0.60		5.45	78.8
BT2		0.1	0.11	1.88	1.26		11.45	85.9

PZT = $Pb_{1.1}(Zr_{0.52}Ti_{0.48})O_3$, M.W. = 346.337 g/mole
BT = $BaTiO_3$,M.W. = 233.21 g/mole
EDTA : M.W. = 292.24 g/mole
NH_3 solution : 35%, specificgravity = 0.88 g/cm^3, M.W. = 17 g/mole
HNO_3 solution : 70%, specificgravity = 1.42 g/cm^3, M.W. = 63 g/mole

The decomposition behaviour was characterised by simultaneous thermal analysis (TG/DTA) carried out from room temperature to 1000°C at a heating rate of 10 deg·min^{-1}. The evolved gas products were analyzed using a mass spectrometer in an air atmosphere. The resultant phases of the precursor after calcination were examined using XRD and TEM microanalysis.

Results

Thermal decomposition behaviour

The nitrate-EDTA precursor

Figure 1 shows the typical DTA/TG curves obtained for the decomposition of the PZT1 and PZT2 gels in air, with a sample weight of 10 mg. 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 weight losses agree well with the values calculated assuming complete loss of all the volatile components (75.5 wt% for the PZT1 gel and 78.0 wt% for the PZT2 gel at 700°C). For the PZT2 gel, 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 weight loss which was virtually complete at an external temperature of 250°C.

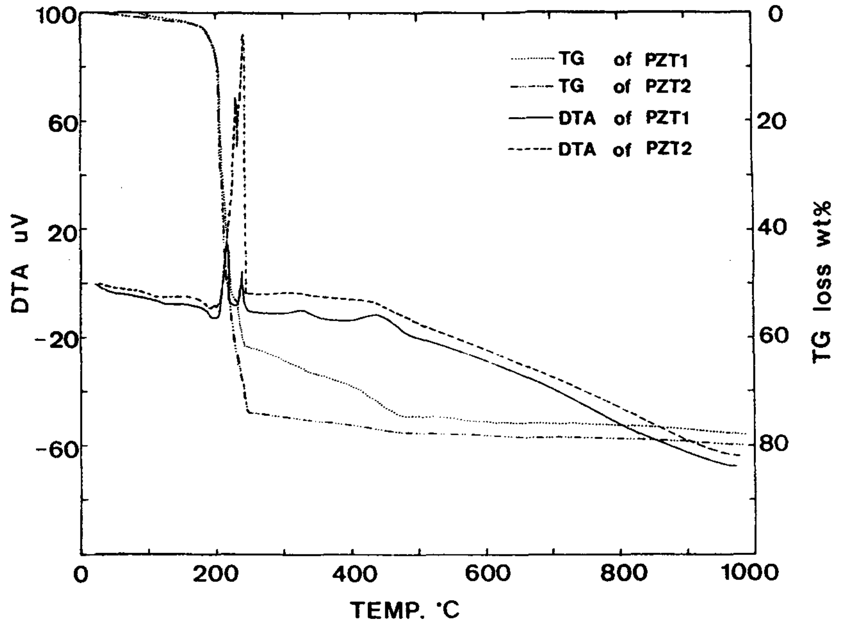

Fig. 1 DTA/TG curves for PZT1 and PZT2 precursors. The total weight losses agree with those calculated on the basis of the amount of volatile material present

The decomposition behaviour of the BT-EDTA gels is quite different, being less sensitive to the nitric acid/EDTA ratio as shown in Fig. 2. The two curves show a similar decompositional behaviour, even though BT2 contains twice the ratio of nitric acid/EDTA used for BT1. The excess nitric acid in the BT2 gel does not give a substantially larger exothermic peak than that of the BT1 gel. A large weight loss is apparent at temperatures below 250°C, but a considerable amount (≥20 wt%) of material remains, giving rise to a further weight loss at higher temperatures. The total weight losses of both BT-EDTA gels (83.5 wt% for the BT1 gel and 88 wt% for the BT2 gel at 800 °C) are a little more than the theoretical predictions (78.8 wt% and 85.9 wt% respectively). In addition, the intensity of the exothermic reaction was much less than that of the PZT-EDTA precursor and the mass loss steps revealed in DTG curves show that there were at least four separated reactions.

The chloride-EDTA precursor

Figure 3 shows the typical DTA/TGA data for thermal decomposition of the chloride-EDTA precursor for PZT powder. It shows a small endothermic reaction close to 200°C and three exothermic reactions at 210, 330 and 490°C. These DTA events are accompanied by a first weight loss at 200°C and gradual

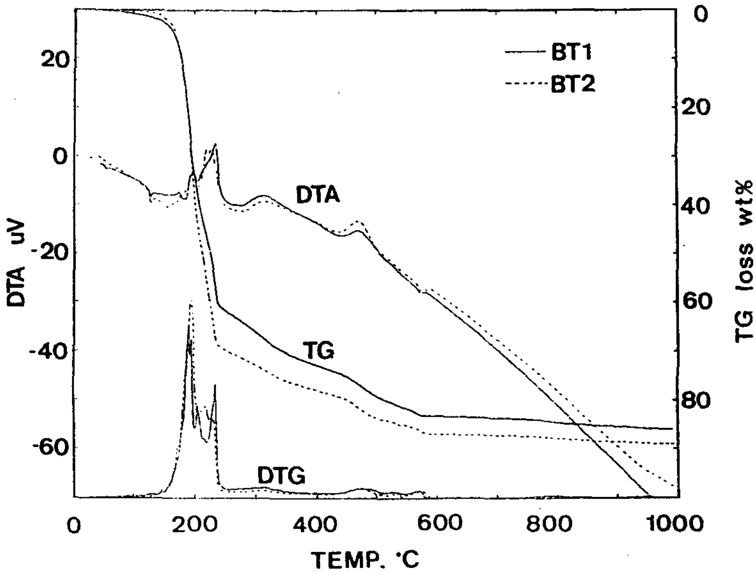

Fig. 2 DTA/TG/DTG curves for BT1 and BT2 precursors. The total weight losses are larger than the predictions

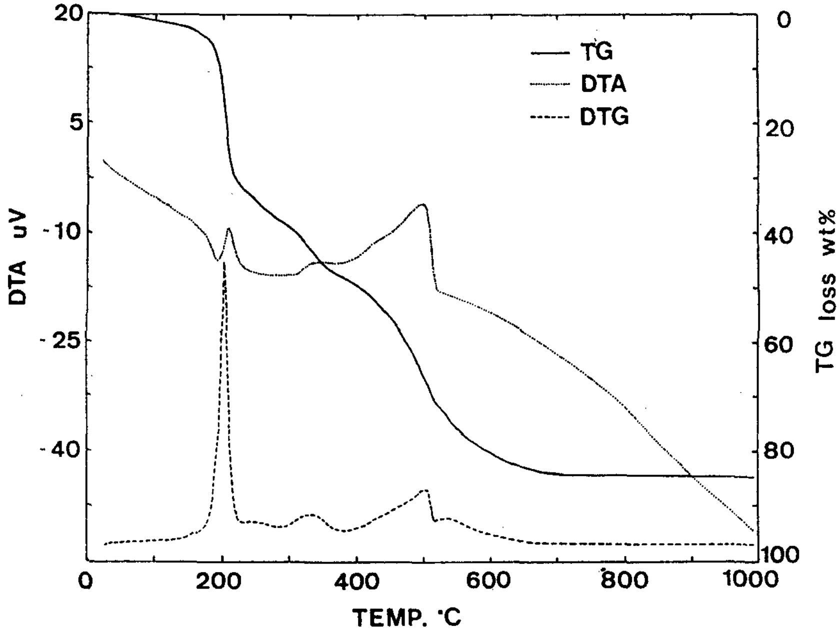

Fig. 3 DTA/TG/DTG curves of chloride-EDTA precursor. The total weight loss is much greater than the prediction

decomposition from 250 to 550°C. The gradual mass loss may be explained by gradual decomposition/oxidation of the organic components. However, the total weight loss (85 wt%) was much greater than that of the theoretical prediction given in Table 1. The DTG curve shows four main mass loss peaks during heating. The positions of the first three exothermic peaks correspond to the exothermic peaks of the nitrate 1 gel in Fig. 1 and are characteristic of the decomposition of the PZT-EDTA precursor. The last weight loss peak in the chloride-EDTA gel is at over 490°C and was not accompanied by any sharp exothermic or endothermic reaction, as shown in Fig. 3. This will be discussed later after the results obtained on examination of the calcined powder in DTA/TG have been presented.

Phase development

The nitrate-EDTA precursors

The sequence of crystalline phases formed during the course of thermal treatment of the PZT2 precursor is shown in Fig. 4 (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 which decomposed to yield gaseous NH_3 and HNO_3 when heated to 200°C. The gaseous ammonia product was confirmed by mass spectrometry. Thus, it is clear that the endothermic peak at 200°C in the DTA curve (Fig. 1) is caused by the decomposition of the ammonium nitrate which was seen to be accompanied by the softening/melting of the solid precursor. Further decomposition and oxidation 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 liberated nitric acid and nitrogen oxides provide an oxidising environment 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. The intermediate $PbTiO_3$ phase, which is often present in materials produced by the mixed oxides method, was not observed.

XRD results for the BT2 precursor are shown in Fig. 5. Both BT-EDTA precursors are similar and agree with the data for the PZT-EDTA precursors. Both BT gels contained two different crystalline forms of NH_4NO_3 as the main crystalline phases. None of the peaks correspond to those of $Ba(NO_3)_2$, indicating that the metal cations are still homogeneously distributed. Formation of crystalline $BaTiO_3$ occurred at temperatures as low as 250°C, but it was accompanied by a just detectable amount of $BaCO_3$ which was stable up to at least 800°C. The presence of carbonates in the powder calcined at 1000°C for 1 h was not detectable by XRD. The BT-EDTA precursor produced a porous and friable powder after calcination at 250°C. This porous matrix transformed into larger crystalline agglomerates after subsequent calcination at higher temperatures in a similar way to the PZT-EDTA precursor.

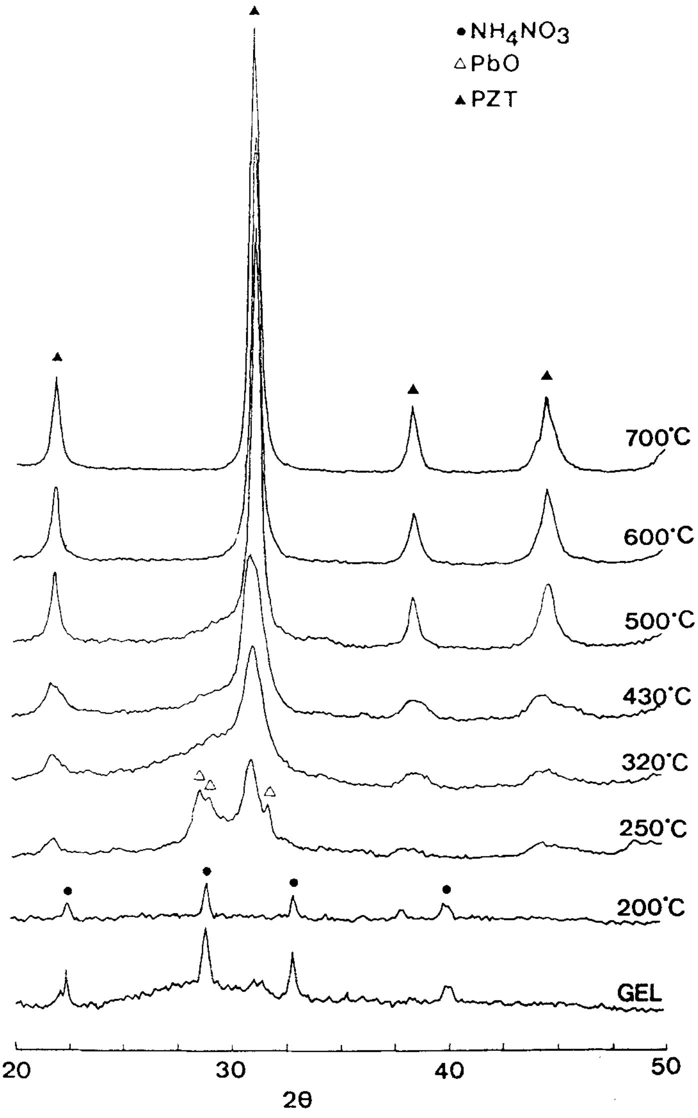

Fig. 4 Phase development of the PZT2 precursor after calcination for 1 h at various temperatures

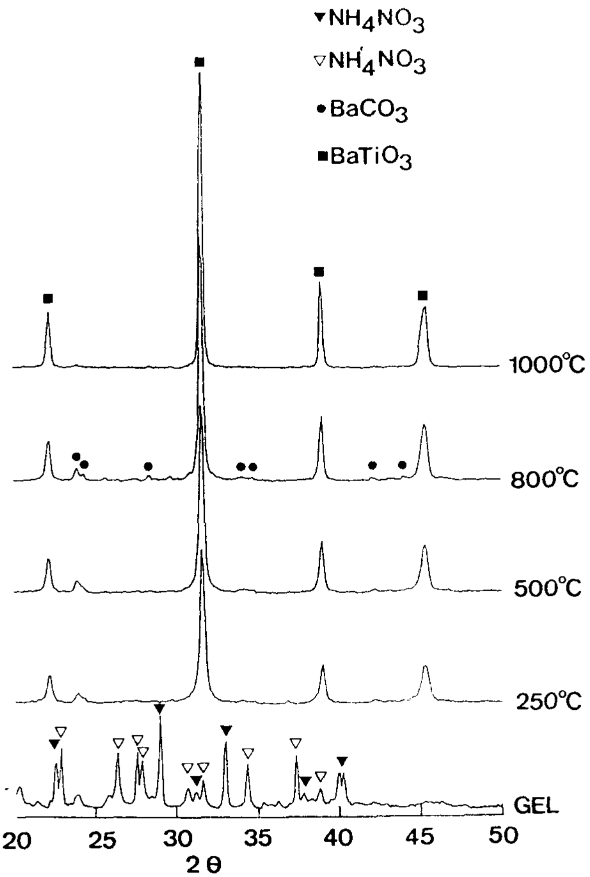

Fig. 5 Phase development of the BT2 precursor after calcination for 1 h at various temperatures

The chloride-EDTA precursor

The XRD results for as-prepared chloride-EDTA precursors and the powders calcined at various temperatures are shown in Fig. 6. There is a minor crystalline phase attributed to NH_4Cl in the chloride-EDTA precursor. However, this is not evident after calcination at 250°C. The endothermic peak at 200°C in the DTA curves (Fig. 3) is most likely caused by the decomposition of this minor crystalline phase and softening/melting of the glassy precursor.

In products obtained after firing at 500°C, evidence of $PbCl_2$ was clear and this compound was the only crystalline phase. The $PbCl_2$ disappeared on further heating to 600°C, at which temperature the first crystalline metal oxide was formed, as shown in Fig. 6. The main peaks corresponded to orthorhombic

$ZrTiO_4$, and not the expected PZT, $PbZrO_3$ or $PbTiO_3$ phases. At 600°C, the $PbTiO_3$ phase first appeared, becoming more clearly evident as the calcination temperature increased.

The chloride-EDTA precursor did not form the desired PZT phase, even after calcination at 1000°C for 1 h, but produced orthorhombic Ti-deficient

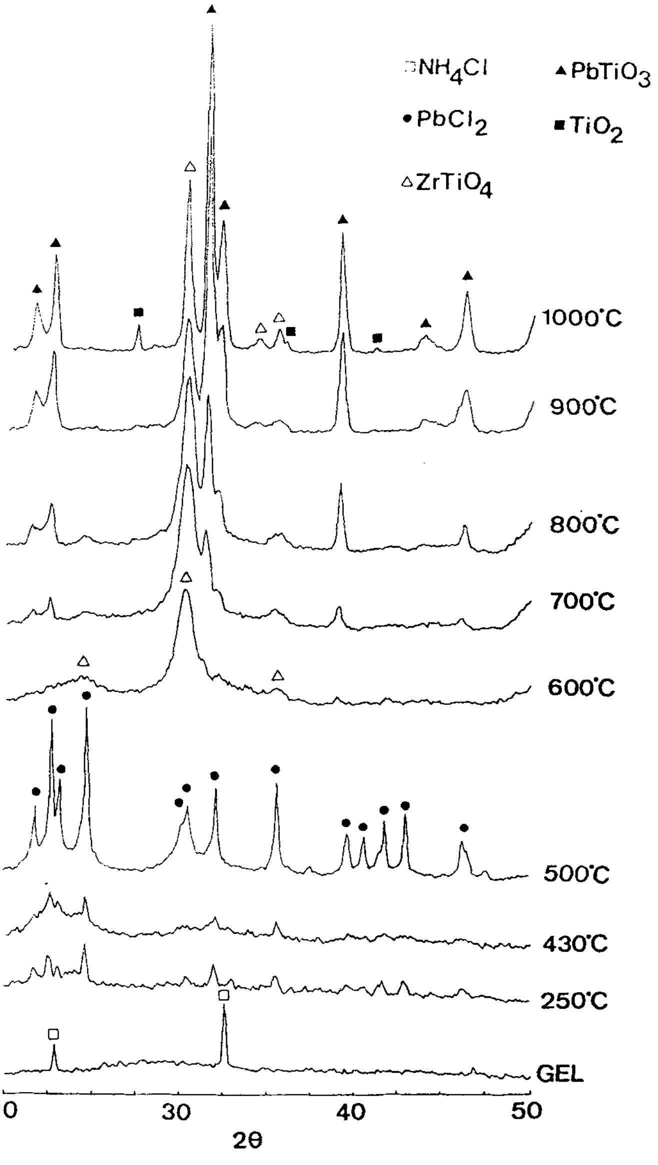

Fig. 6 Phase development of the chloride-EDTA precursor after calcination for 1 h at various temperatures

$ZrTiO_4$, rutile TiO_2 and $PbTiO_3$. The *c/a* ratio of the resultant lead titanate phase (1.052) is less than that of pure $PbTiO_3$ (1.064), indicating that some Zr is present in solid solution, and the (111) main peak of $ZrTiO_4$ ($d_{111} = 2.93$A, $2\Theta = 30.45°$) is shifted slightly to a lower angle due to the titanium-deficiency.

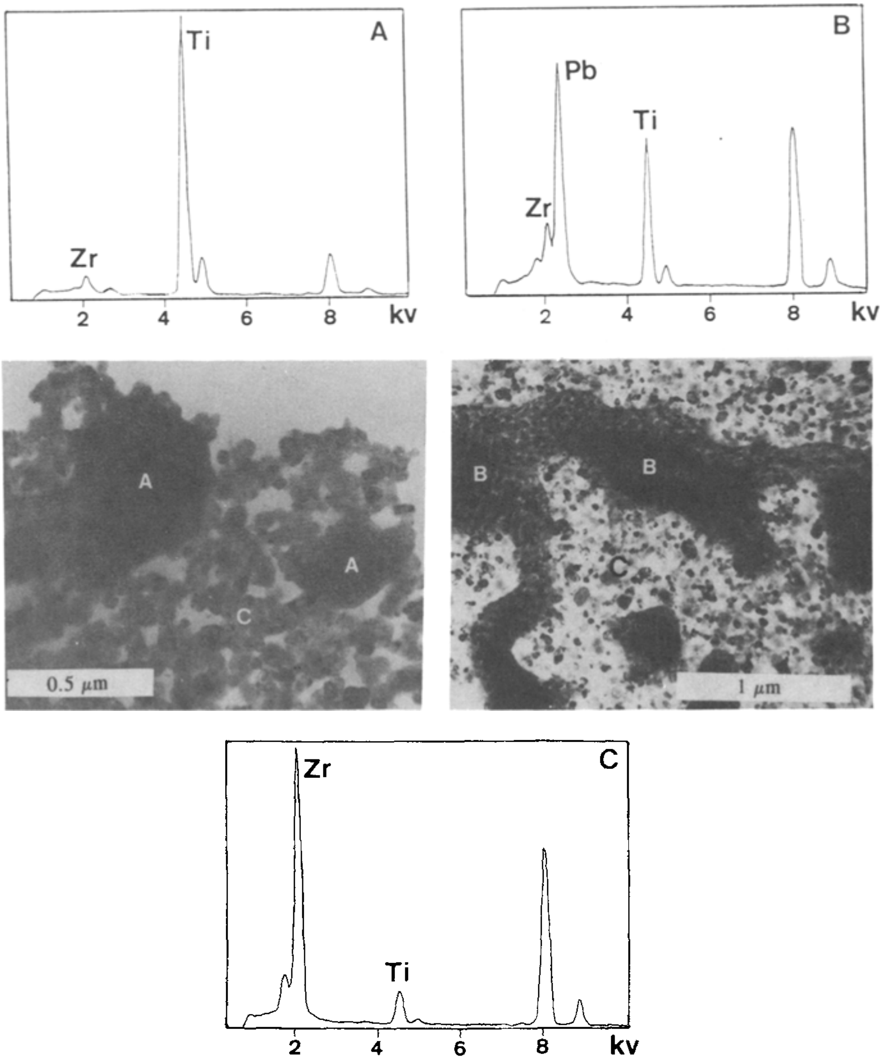

Fig. 7 TEM micrograph with EDX spectra shows the phase segregation in calcined powder derived from the chloride-EDTA precursor at 1000°C. Region A = TiO_2, region B = $PbTiO_3$, region C = $ZrTi_{1-(3/2)x}O_{4-3x}$

The compositional segregation in the chloride-EDTA derived powder calcined at 1000°C for 1 h was further confirmed using nanoprobe EDX down to 20 nm in the TEM, as shown in Fig. 7. Here, three types of particle morphology can be seen in the powder. Large cubic particles (region A), which are occasionally found isolated but dispersed within the finer particles, are mainly Ti containing, indicating that these are TiO_2. The dark, strongly diffracting, smoothly-contoured particles, denoted as B in Fig. 7, comprise a Zr-containing $PbTiO_3$ phase. The very fine particles (region C), which are less than 0.1 μm in size, were identified as ZrO_2 with some Ti. These fine (C) and cubic (A) particles were completely lead free, as shown in the EDX spectra.

It is clear that there are at least three phases in the chloride-EDTA derived powder calcined at 1000°C for 1 h, which may be identified as TiO_2, Ti-deficient $ZrTiO_4$, and $PbTiO_3$ (containing some Zr). The development of these phases is discussed below.

Evolved gas analysis (EGA)

The results of EGA by mass spectrometry indicate that the gaseous products were NH_3, H_2O, NO and CO_2. Figures 8 and 9 show the evolved gases during thermal decomposition for the PZT2 and BT2 gels, respectively. The four gaseous products were evolved from 200 to 240°C for the PZT2 gel and from 170 to 250°C for the BT2 gel. However, the ratios of the quantities of these gases, given in Table 2, are quite different for these two gels. The gaseous products from PZT2 are of the same order of magnitude. But, in the BT2 precursor the amount of water is much greater than that of the three other gaseous products. This gives a clear idea why the exothermic heat is so small in BT-EDTA precursors. It also suggests that the BT-EDTA precursors incorporated a lot of water. Furthermore, the gaseous products of both EDTA precursors are similar to those observed in the decomposition of amorphous citrate gels, suggesting that a similar reaction scheme may be involved.

Discussion

The nitrate-EDTA precursor

The sharp exothermic reaction and weight loss of the PZT-EDTA precursor at temperatures around 240°C may be explained in terms of the exothermic reaction between nitric acid and EDTA, and the following spontaneous combustion of the organic component. A higher molar ratio of nitric acid to EDTA resulted in more complete decomposition of the gel. Crystallisation of the PZT

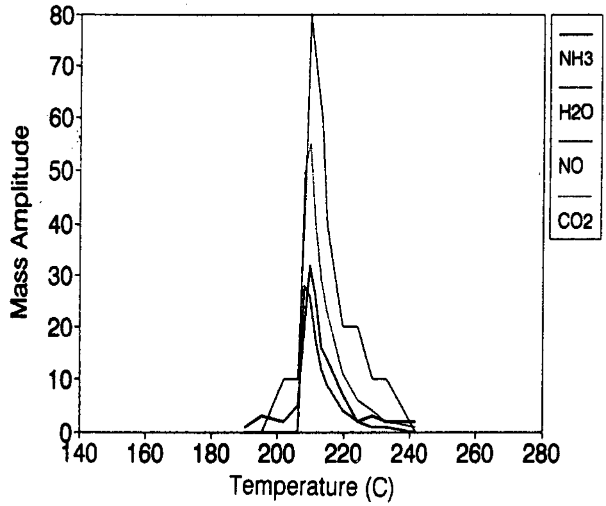

Fig. 8 Evolved gas analysis of PZT2 precursor

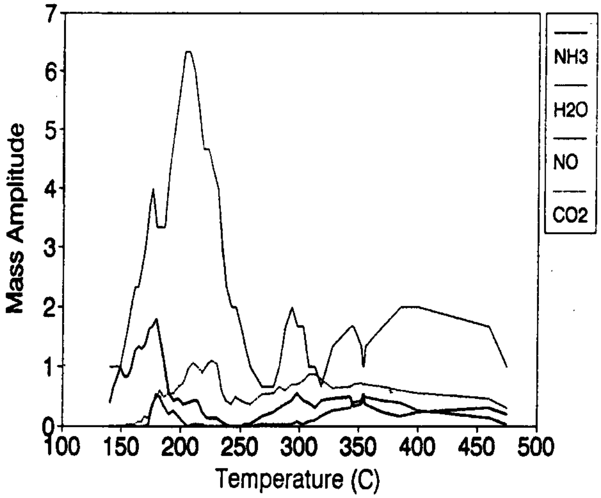

Fig. 9 Evolved gas analysis of BT2 precursor

Table 2 Evolved gas quantity ratio/%

Precursor	NH_3	H_2O	NO	CO_2	Evolved temp./°C
PZT2 gel	16.2	44.8	12.2	26.8	200–240
BT2 gel	7.9	75.2	5.5	11.4	170–250

phase initiated when enough heat was generated by this exothermic reaction, though the external temperature was only ≈250°C.

The decomposition behaviour of the BT-EDTA precursors are distinguished from those of PZT-EDTA precursors by their small exothermic reaction at 210–240°C and the separated loss steps as shown in the DTG curve (Fig. 2). A large amount of residual carbon is left in the BT-EDTA derived powder due to incomplete oxidation of the organic part of the gel and the formation of $BaCO_3$. The total weight loss of the BT-EDTA gel precursors was 2–4 wt% more than that predicted.

Two factors may be involved for the small exothermic reaction at 210°C, despite the high nitrate/EDTA ratio of BT gels. First, the BT-EDTA precursors incorporated excess water as revealed by evolved gas analysis. For any given set of decomposition conditions, it would be necessary for this chemically-bonded water to be removed, resulting in an overall less intensive exothermic reaction and possible incomplete oxidation. The observed weight changes for the BT1 and BT2 gels suggest a value of $x \approx 15$–20 in a complex BT-EDTA·xH_2O. It is this decomposition and evaporation of water that reduces the intensity of the main exothermic reaction. The value is somewhat larger than the incorporated water in EDTA complexes reported in the literature [13, 14], which have been shown to occur with up to 10 molecules of water to one of EDTA.

Secondly, the formation of barium carbonate in BT-EDTA precursors cannot be ignored. The formation of carbonate reduces the amount of carbon in the carbonaceous char and hence decreases the exothermic oxidation. From this point of view, elements such as Sr and Ca may affect the decompositional behaviour in a similar manner.

Mechanism of phase segregation in chloride precursors

Yoshikawa and Tsuzuki [15] have confirmed that lead monoxide is required to form the lattice of the perovskite structure of PLZT. Such initial formation of PbO at low temperature (300°C) has also been demonstrated in the preparation of PZT ceramic powder by the alkoxide route [16]. Therefore, it is assumed that the absence of PbO in the calcined powder obtained from the chloride-EDTA precursor could be a primary reason for absence of the PZT phase. The absence of PbO in the chloride-EDTA derived powder is due to the formation of $PbCl_2$, which was found to be stable until 600°C, above which is started to react with the $ZrTiO_4$ which had formed because of the absence of PbO.

According to the XRD data, traces of $PbTiO_3$ were formed initially at 600°C but this phase only became clearly evident at higher temperatures. However, $ZrTiO_4$ was present in abundant quantities at 600°C and above. As a result, it seems likely that the titanium ions which eventually produce the significant quantities of $PbTiO_3$ at higher temperatures must come from $ZrTiO_4$ which coexists in the region 500–600°C with $PbCl_2$. A possible reaction between $PbCl_2$ and $ZrTiO_4$ is as follows:

$$x\,PbCl_2 + ZrTiO_3 \rightarrow x\,PbTiO_3 + ZrTi_{1-3/2x}O_{4-3x} + \frac{x}{2}\,TiCl_4$$

The titanium tetrachloride will volatilize and hydrolyze/oxidize further to form titanium oxide during subsequent calcination.

According to the suggested reaction above, x can vary from 0 to 2/3, and the remaining lead chloride (1.533 mole) of the original precursor stoichiometry cannot be accounted for. However, the results shown in Fig. 10 indicate that the unreacted lead chloride is lost as a vapour. The TG curves of powder from the chloride-EDTA precursor calcined at 500 and 600°C show an unexpected weight loss from 500 to 700°C. The only crystalline phase in the powder produced at 500°C was lead chloride (Fig. 6). Figure 10 shows a melting peak at 483°C which is associated with the lead chloride, and a broad endothermic reaction around 640°C in the DTA curve. This latter endothermic reaction has an associated large weight loss of 58 wt% in the TG curve (for the powder calcined at 500°C).

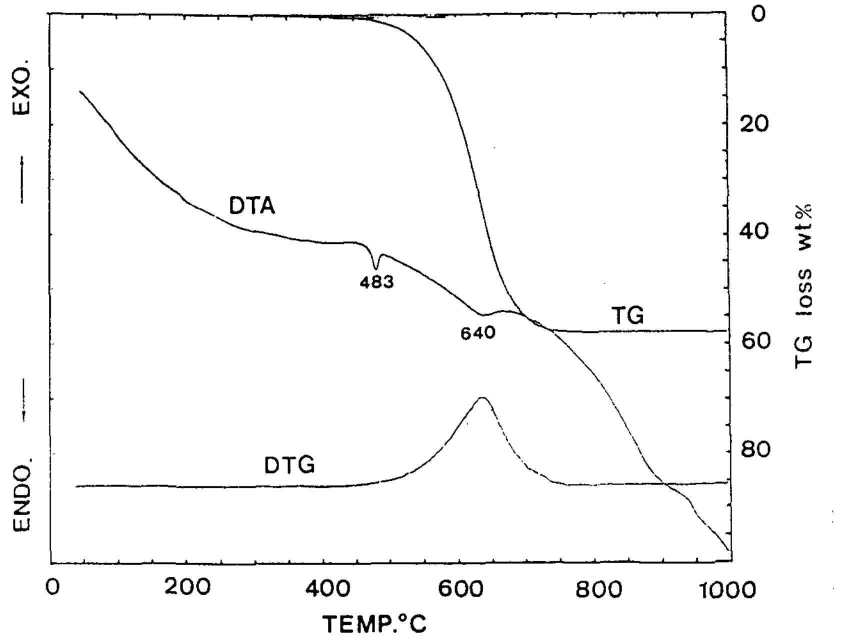

Fig. 10 DTA/TG/DTG curve of calcined derived from chloride-EDTA precursor at 500°C/1 h. The 58 wt% loss of 500°C-calcined powder agrees with the proposed reaction mechanism

These thermoanalytical data indicate that the unreacted lead chloride was gradually evaporated after melting. A theoretical calculation of weight loss for the powder calcined at 500°C gives a value of 56.7 wt% for the loss of unreacted lead and all chloride ions (including the weight change due to the formation of TiO_2). This value was obtained by taking $x_{max} = 2/3$ in the suggested reaction. If x was less than this maximum value, it should give a greater weight loss due to the greater amount of unreacted $PbCl_2$. These calculations show a good agreement with the observed total weight loss of 58 wt% for this powder.

Conclusions

1. Fine, homogeneous ceramic powders were prepared by the metal nitrate-EDTA gel process. The calcination temperatures employed were substantially lower than those required in the conventional routes. The nitrate ions provided an 'in-situ' oxidising environment for the decomposition of the organic component, and the subsequent heat evolution facilitated the crystallization of the PZT and BT phases at a very low external temperature (≈250°C).
2. Phase segregation in the chloride-EDTA precursor was found to be due to the formation and subsequent evaporation of $PbCl_2$. The suggested reaction which was proved by DTA/TG analysis explained the detailed weight changes and phase segregation.

References

1 D. J. Anderton and F. R. Sale, Powder Metall., 22 (1979) 14.
2 M. S. G. Baythoun and F. R. Sale, J. Mater. Sci, 17 (1982) 2757.
3 F. R. Sale and F. Mahloojchi, Ceram. Internat., 14 (1988) 229.
4 H. W. Wang, D. A. Hall and F. R. Sale, J. Amer. Ceram. Soc., 75 (1992) 124.
5 J. Fransaer, J. R. Roos, L. Delaey, O. Van Der Biest, O. Arkens and J. P. Celis, Appl. Phys., 65 (1989) 3277.
6 F. H. Chen, H. S. Koo and T. Y. Tseng, J. Amer. Ceram. Soc., 75 (1992) 96.
7 P. Courty, H. Ajot, C. Marcilly, and B. Delmon, Powder Technol., 7 (1973) 21 (In French).
8 B. Delmon and J. Droguest, 'Some Mechanistic Features of the Amorphous Citrate Process' Second Int. Conf. on Fine Particles, eds. W. E. Kuhn and J. Ehretsmann, Electrochemical New Jersey, 1973, p. 242.
9 D. Hennings and W. Mayr, J. Solid State Chem., 26 (1978) 329.
10 H. W. Wang, D. A. Hall and F. R. Sale, J. Thermal Anal., invited paper.
11 Y. Yoshikawa, K. T. T. Kobayashi and A. Takagi, J. Mater. Sci., 23 (1988) 2729.
12 J. M. Wu and H. W. Wang, J. Amer. Ceram. Soc., 71 (1988) 869.
13 R. H. Nuttall and D. M. Stalker, Talanta, 24 (1977) 355.
14 M. D. Lind, B. Lee and J. L. Hoard, J. Amer. Chem. Soc., 5 (1965) 1611.
15 Y. Yoshikawa and K. Tsuzuki, J. Europ. Ceram. Soc., 6 (1990) 227.
16 M. E. Dawes and A. J. Moulson, British Ceramic Proceedings, 38 (1986) 111.

Zusammenfassung — Man fand, daß Rohchemikalien wie z.B. Metallnitrate und -chloride das thermische Zersetzungsverhalten von EDTA-Gelpräkursoren für die Herstellung von Keramikpulvern beeinflussen. Aus Nitratlösungen wurden feine, homogene Keramikpulver gefertigt, während Chloride segregierte Phasen ergeben. In einer Untersuchung an der Fertigung von Bleizirkonattitanat (PZT) unter Einsatz von Chloriden wurde eine Entmischung und der Verlust von Blei beobachtet und als Grund dafür die Bildung und Verdampfung von $PbCl_2$ ermittelt. Mittels DTA/TG konnte der vorgeschlagene Reaktionsmechanismus für diese Phasenentmischung quantitativ bekräftigt werden. Die Kristallisation der gewünschten Perovskit-Phase von Bleizirkonattitanat (PZT) und Bariumtitanat (BT) setzte bei den Nitrat-EDTA Präkursoren bei so niedrigen Temperaturen wie 250°C ein. Kristallwasser und die Bildung von $BaCO_3$ im Bariumtitanat-Präkursor werden für die Unterschiede im beobachteten Zersetzungsverhalten der Präkursoren BT und PZT verantwortlich gemacht.