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The use of TGA-MS, TGA-FTIR, HT-XRD and HT-DRIFT for the preparation and characterization of $PbTiO_3$ and $BaTiO_3$

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Abstract

Our research is focused on the preparation and characterization of promising multimetal oxide ceramic materials, such as superconducting cuprates and ferroelectric materials. Results of the sol–gel synthesis of two compounds are discussed: $PbTiO_3$ (PTO) and $BaTiO_3$ (BTO). These are important products in the study of ferroelectric materials, with interesting applications as non-volatile ferroelectric random access memories (NVFRAMs), such as $PbZr_{1-x}\ Ti_xO_3$ (PZT) and BTO-stabilized $PbZn_{1/3}\ Nb_{2/3}O_3$ (PZN).

The aim of this presentation is to show how the combination of TGA-evolved gas analysis (TGA-EGA) (i.e. mass spectrometry (MS) and Fourier transform infrared spectroscopy (FTIR) on-line coupled to TGA) gives important, but not sufficient, information for a complete identification of the intermediates that are formed during thermal decomposition. By using TGA-EGA, these intermediates can only be determined indirectly by calculation from the weight losses or by the identification of the evolved gasses. Direct information about the intermediates and the final decomposition products can be obtained by in situ high-temperature-X-ray diffraction (HT-XRD) and high-temperature-diffuse reflectance FTIR (HT-DRIFT) measurements during heat treatment.

Keywords: Sol–gel; $PbTiO_3$; $BaTiO_3$; TGA-EGA; HT-XRD; HT-DRIFT

1. Introduction

Traditionally, ceramic multimetal oxides are prepared by heating mechanically mixed starting compounds, mostly oxides or carbonates. In such a dry synthesis method, repeated grinding and heating is required resulting in long calcination and sintering times, as the metal ions have to travel over thousands of unit cells before reaching the right position in the lattice. The search for new products by doping and substitution of elements implies extreme homogeneity of the multimetal system. Chemical precursor routes start from a solution in which the materials are already mixed at an atomic level. An important advantage of the so-called wet techniques is the fact that the formation of secondary phases is minimized because local variations of the stoichiometry in the precursor are more unlikely to happen. The distance over which the metal ions have to travel during the thermal treatment to reach their position in the crystal lattice is shorter, leading to shorter heating times at lower temperatures. Moreover, the chemical precursors are very suitable for making various shapes, such as films, fibres and wires.

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In our laboratory, different chemical preparation techniques such as coprecipitation–filtration [1–5] and sol–gel synthesis [6,7] are used for the preparation of precursors for various multimetal oxides. For the study of the transition of the precursors into the final products, the combination of a variety of thermal analysis methods is indispensable.

2. Experimental

$PbTiO_3$ (PTO) was prepared using lead(II)acetate trihydrate (Merck p.a.), titanium(IV)isopropoxide (Janssen Chimica, >98%), 2-butoxy ethanol (Janssen Chimica, 99%) and di-ethanol amine (Aldrich, 99%). As could be proven by TGA-mass spectrometry (TGA-MS), lead(II)acetate trihydrate was made water-free in the solid state by re-crystallization of the hydrated lead acetate from 2-butoxy ethanol and by washing with ethanol and di-ethyl ether. The water-free lead acetate and the Ti(IV)isopropoxide were dissolved in an equimolar solution of butoxy ethanol and di-ethanol amine. Without di-ethanol amine as a complexing agent, the lead acetate is insoluble in the alcohol. After refluxing at 130 °C for 6 h, the mixture was vacuum distilled to remove the esters that were formed between the acetate and the alcohol. After addition of an amount of solvent, partial hydrolysis and condensation was performed by adding a small amount of nitric acid and water and by heating the mixture at 70 °C until a viscous sol of the PTO precursor was obtained. A homogeneous amorphous precursor gel is obtained after evaporation. The perovskite-type crystalline structure with maintenance of the homogeneous cation distribution is formed by the thermal decomposition of the precursor at about 500 °C. An analogous recipe with isopropanol instead of butoxy ethanol and with various alkanol amines has been published earlier by Kim et al. [8]. Blum and Gurkovich synthesized PTO, starting from lead acetate and Ti(IV)isopropoxide [9,10].

$BaTiO_3$ (BTO) was prepared by thermal treatment of an aqueous citrate precursor. This precursor was prepared by adding bariumacetate (Aldrich, 99%) to a Ti(IV)peroxocitrato precursor at pH 8.5 (pH adjusted by adding ammonia). In comparison with the synthesis of the Nb(V)peroxocitrato precursor of Narendar and Messing [11], the Ti(IV)peroxocitrato precursor solution was prepared by adding citric acid (Aldrich, 99%) and hydrogen peroxide (Acros, 35 wt.% solution in H_2O p.a.), both in a proportion 2:1 against Ti(IV), to an aqueous precipitate prepared by hydrolyzing Ti(IV) isopropoxide (Acros, >98 %) in water. After evaporation, a homogeneous amorphous precursor gel is obtained. By thermal treatment, the gel is transformed into the perovskite-type crystalline structure at 700 °C. Techniques with the intention of preparing nanoparticles (around 50 nm) of BTO have been used by others, such as a hydrothermal method by Choi et al. [12] and coprecipiation methods by Pfaff [13] and by Saegusa et al. [14].

The thermal behavior is studied by means of TA instruments TGA 951-2000 on-line coupled with a Bruker IFS 48 FTIR spectrometer. The working condition of the TGA was checked with the copper oxalate test [15]. For the on-line coupling TGA-MS, a quadrupole mass spectrometer Thermolab VG Fisons was used, operating with a flexible heated silica lined steel capillary and a molecular leak [16]. Complementary on the evolved gas analysis by TGA-Fourier transform infrared spectroscopy (TGA-FTIR) and TGA-MS, high-temperature-diffuse reflectance FTIR (HT-DRIFT) (Bruker IFS66) and high-temperature-X-ray diffraction (HT-XRD) (Siemens D5000) were used to analyze in situ changes during the transformation of the precursor gel into the final oxide.

3. Results and discussion

3.1. Thermal decomposition of the $PbTiO_3$ precursor

Figs. 1 and 2 show the TGA-FTIR results of the precursor gel of PTO in dry air at a heating rate of 10 °C/min.

The evolution of specific gasses as a function of time or temperature is followed (Fig. 2) by the integration of the spectral intensities at the following characteristic wave number ranges (FTIR-windows): CO_2, 2266–2413 cm^{-1}; C–O–C (ether, secondary alcohol), 1169–1090 cm^{-1}; O–H (alcohol), 3702–3603 cm^{-1}; C–O (alcohol), 1089–1004 cm^{-1}; C=O (carbonyl: ester, aldehyd, ketone,...), 1818–1712 cm^{-1}; NH_3, 932 + 968 cm^{-1}.

The on-line combination TGA-FTIR, shows that alcohols, ethers and carbonyl compounds are released

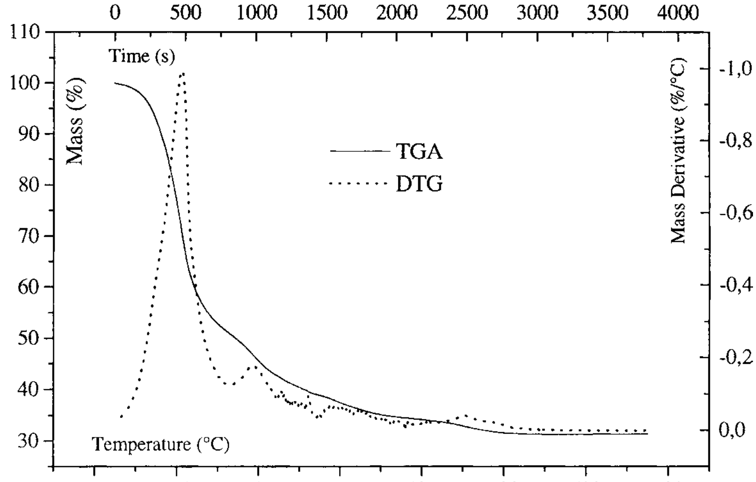

Fig. 1. TGA of the PTO precursor in dry air at 10 °C/min.

mainly untill about 1500 s (275 °C). It is well known that alcohols, ethers and esters can be formed during the formation of oxobridges M–O–M, as a result of the condensation that takes place due to the thermal treatment, as has been described elsewhere for analogous precursors [17,18]. The decomposition of di-ethanol amine is clearly shown by the simultaneous formation of CO_2 and NH_3 with a maximum at about 2000 s (350 °C). This is higher than the boiling point of pure di-ethanol amine (269 °C) due to the complexing property of this alkanol amine in the gel. Finally, the oxide is obtained at about 500 °C.

3.2. Formation of the $BaTiO_3$ precursor

HT-XRD is used to follow in situ the formation of the BTO oxide out of the BTO precursor gel (see Fig. 3). The XRD spectra of the precursor are taken during heating of the sample at 10 °C/min in dry air. The intense peaks at 2θ values of about 40, 46 and 67

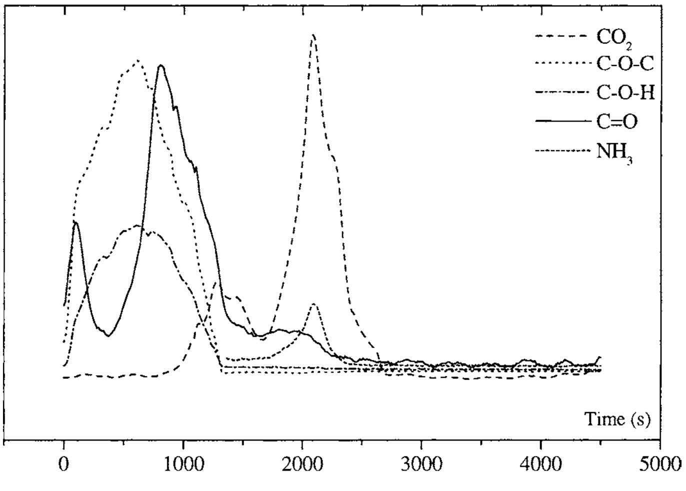

Fig. 2. FTIR-windows: evolution of the evolving gasses released by the $PbTiO_3$ precursor during heating up in dry air at 10 °C/min.

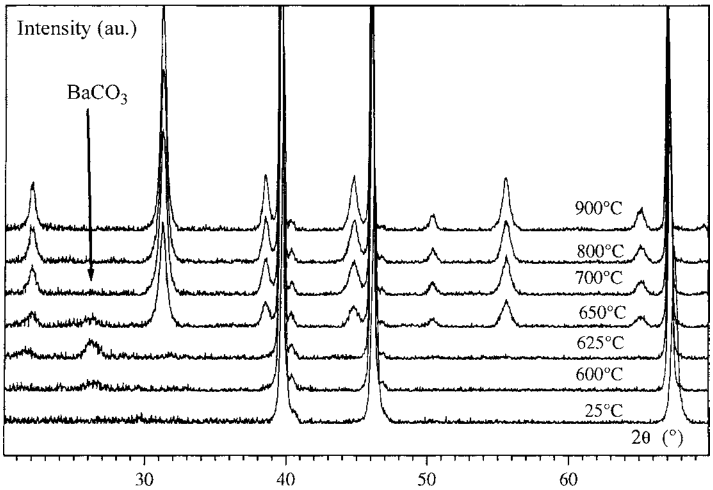

Fig. 3. HT-XRD of the $BaTiO_3$ precursor in dry air at 10 °C/min.

result from the Pt sample holder. From the spectra, it can be clearly seen that some barium carbonate is formed during the decomposition of the precursor into the oxide. This carbonate decomposes between 650 and 700 °C, which is much lower than that for pure $BaCO_3$. At 700 °C, pure BTO oxide is obtained.

Fig. 4 shows the evolution of the emission of CO_2 during the heating of the precursor: MS on-line coupled to TGA. The CO_2-evolution between 600 and 700 °C corresponds to the decomposition of the carbonate. As in the case of the PTO precursor (Fig. 2), of course, a variety of gasses evolves. In this case, cyclic anhydrides (typical for citric acid decomposition), ammonia, water, etc. evolve during the condensation of the precursor gel.

In situ HT-DRIFT measurements provide additional direct information about the intermediates that are formed during heating of the BTO precursor in dry air. The results are presented in Fig. 5. One can distinguish several vibrational characteristic absorptions for the metal citrate precursors.

The broad band at 1075 cm^{-1} is due to the (alcoholic) C–O stretch coming from coordinated α-hydroxy groups (C–O–metal) and non-coordinated α-hydroxy

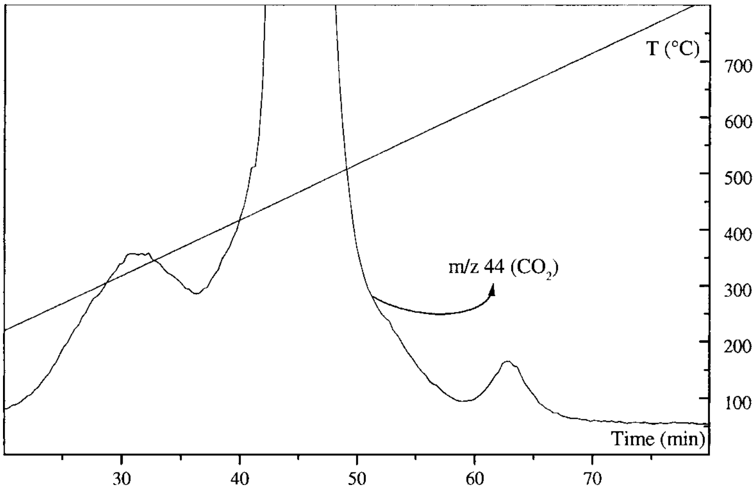

Fig. 4. Emission of carbon dioxide during heating of the $BaTiO_3$ precursor in dry air at 10 °C/min (TGA-MS).

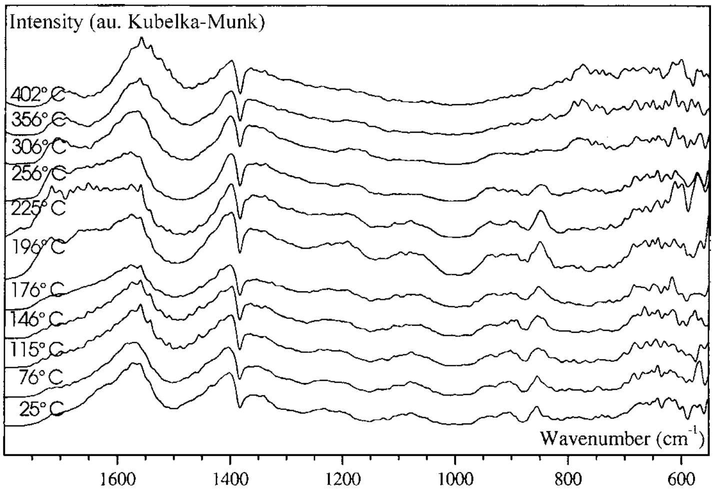

Fig. 5. HT-DRIFT of the $BaTiO_3$ precursor in dry air at 10 °C/min.

groups (C–O–H). At low-temperatures (150 °C), the latter dehydrolyses [19]. At elevated temperature (306 °C), the absorption of the (alcoholic) C–O–metal disappears, indicating the decomposition of the bond between the metal ion and the α-hydroxy group of the citrate.

The carbon stretching of metal-carboxylate-like species is observed around 1405 and 1570 cm^{-1}. To be able to measure these precursors in the HT-DRIFT-mode at even higher temperatures (above 400 °C), experiments were carried out in non-oxidative atmosphere. Fig. 6 shows the thermal decomposition of the BTO precursor in N_2 (10 °C/min). Here, we can clearly observe the formation of $BaCO_3$ above 500 °C (broad band at 1500 cm^{-1}). It is even possible to see the adsorbed gasses formed during the thermal decomposition. The vibrational absorption at 2200–2150 cm^{-1} is due to the formation of CO.

The formation of $BaCO_3$ is attributed to carbon dioxide resulting from the decomposition of the citric acid precursor. To verify that the equipment contains no carbon dioxide coming from outside, the copper oxalate test, as described elsewhere [15], is performed for the HT-DRIFT equipment. Fig. 7 shows no vibrational

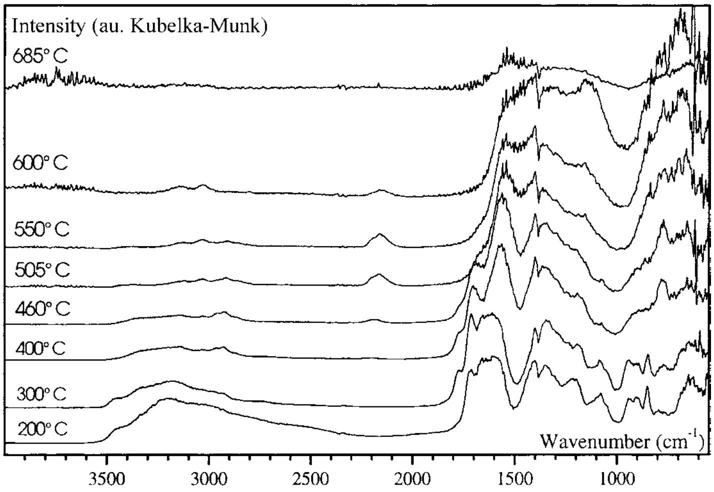

Fig. 6. HT-DRIFT of the $BaTiO_3$ precursor in N_2 at 10 °C/min.

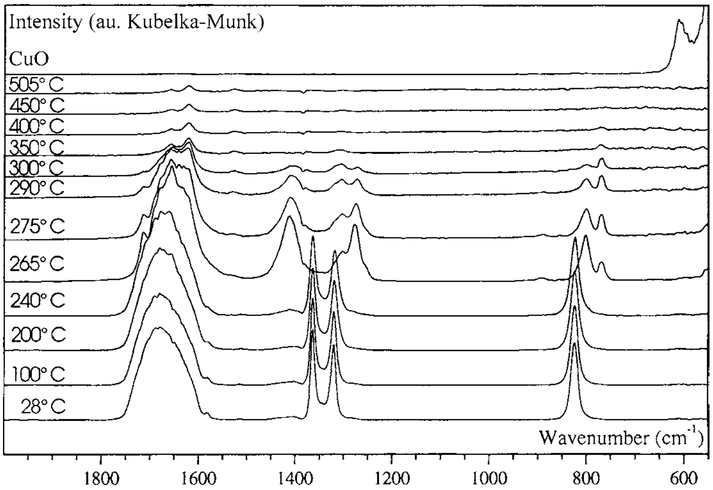

Fig. 7. HT-DRIFT of copper oxalate in N_2 at 10 °C/min. The upper spectrum of CuO is used as a guide to distinguish CuO-formation.

absorptions of CuO after decomposition of the oxalate. The resulting product is clearly copper, since the processed material shows typical Cu(0)-features after cooling (reddish color). This means, there is no dead volume in the equipment containing air, nor a leak through which air can enter during the experiment.

4. Conclusion

Although the combination of TGA with identification of the evolved gasses using on-line coupling of TGA with MS and FTIR gives important information about the decomposition reactions, the intermediate reaction products can only be determined indirectly by calculation from the weight losses, or by the identification of the evolved gasses. If the products are crystalline, HT-XRD is very suitable for in situ identification of the decomposition products during heating. The combination of TGA-EGA with HT-DRIFT also allows in situ identification of the intermediate decomposition products from their IR-active groups even when they are amorphous products.

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References

[1] A. Vos, R. Carleer, J. Mullens, J. Yperman, J. Vanhees, L.C. Van Poucke, Eur. J. Solid State Inorg. Chem. 28 (1991) 657.
[2] J. Mullens, A. Vos, A. De Backer, D. Franco, J. Yperman, L.C. Van Poucke, J. Thermal. Anal. 40 (1993) 303.
[3] E. Knaepen, J. Mullens, J. Yperman, L.C. Van Poucke, Thermochim. Acta 284 (1996) 213.
[4] I.I. Schildermans, M.K. Van Bael, E. Knaepen, J. Yperman, J. Mullens, L.C. Van Poucke, Physica C 278 (1997) 55.
[5] G. Vanhoyland, R. Nouwen, M.K. Van Bael, J. Yperman, J. Mullens, L.C. Van Poucke, Thermochim. Acta 354 (2000) 145.
[6] M.K. Van Bael, E. Knaepen, A. Kareiva, I. Schildermans, R. Nouwen, J. D'Haen, M.D. Olieslaeger, C. Quaeyhaegens, D. Franco, J. Yperman, J. Mullens, L.C. Van Poucke, Supercond. Sci. Technol. 11 (1998) 82.
[7] M.K. Van Bael, A. Kareiva, R. Nouwen, I. Schildermans, G. Vanhoyland, J. D'Haen, M. D'Olieslaeger, D. Franco, J. Mullens, J. Yperman, L.C. Van Poucke, Int. J. Inorg. Mater. 1 (1999) 259.
[8] S.H. Kim, C.E. Kim, Y.J. Oh, J. Mater. Sci. 30 (1995) 5639.
[9] J. Blum, S. Gurkovich, J. Mater. Sci. 20 (1985) 4479.
[10] S. Gurkovich, J. Blum, Ferroelectrics 62 (1985) 189.
[11] Y. Narendar, G.L. Messing, Chem. Mater. 9 (1997) 580.

[12] G.J. Choi, H.S. Kim, Y.S. Cho, Mater. Lett. 41 (1999) 122.

[13] G. Pfaf, J. Mater. Sci. 27 (1992) 1222.

[14] K. Saegusa, W.E. Rhine, H.K. Bowen, J. Am. Ceram. Soc. 76 (1993) 1495.

[15] J. Mullens, A. Vos, R. Carleer, J. Yperman, L.C. Van Poucke, Thermochim. Acta 207 (1992) 337.

[16] J. Mullens, Evolved gas analysis, in: M. Brown (Ed.), Handbook of Thermal Analysis and Calorimetry, Vol. I, Principles and Practice, Elsevier, Amsterdam, 1998 (Chapter 12).

[17] C.J. Brinker, G.W. Scherer, Sol–Gel Science, Academic Press, San Diego 1990, p. 43.

[18] R. Nouwen, J. Mullens, D. Franco, J. Yperman, L.C. Van Poucke, Vibrat. Spectrosc. 10 (1996) 291.

[19] M. Rajendran, M. Subba Rao, J. Solid State Chem. 113 (1994) 239.