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Study of the decomposition of an aqueous metal–chelate gel precursor for $(Bi,La)_4Ti_3O_{12}$ by means of TGA–FTIR, TGA–MS and HT-DRIFT

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Abstract

A $(Bi,La)_4Ti_3O_{12}$ acetate–citrate gel, prepared from an aqueous solution, was subjected to thermal decomposition in dry air and in inert atmosphere. In order to acquire the insight into its decomposition pathway, several hyphenated thermal analysis techniques were used. The evolved gases were characterized by TGA–MS and TGA–FTIR, while any changes in the solid phase upon heating were detected by means of HT-DRIFT.

In dry air, the decomposition consists of four steps, centered at 80, 190, 340 and 455 °C. After drying of the sample in the first step, the second step is ascribed to the decomposition of ammonium acetate and citrate. Any metal acetates present in the gel would also decompose here. The third step comprises the decomposition/combustion of the citrate ligands. The last step consists of the combustion of all residual organic matter. In the third and fourth step, O_2 plays an important role. XRD has proven that the desired Aurivillius oxide phase forms from the synthesized gel after an appropriate heat treatment in dry air.

In inert atmosphere six steps can be distinguished, situated at 70, 200, 330, 420, 590 and 910 °C. The steps at 70, 200 and 330 °C correspond to the steps at 80, 190 and 340 °C in dry air. It is proposed that the steps above 400 °C correspond to the gradual decomposition of the residual organic matter. It has turned out to be impossible to remove all organic matter from the gel below 700 °C in inert atmosphere.

Keywords: BLT; TGA–EGA; HT-DRIFT; Ferroelectric; Gel synthesis

1. Introduction

Bismuth titanate ($Bi_4Ti_3O_{12}$, BIT) is a ferroelectric material with a layered perovskite-like structure (Aurivillius) and a very high Curie temperature of 675 °C. One of its possible applications lies in the field of the ferroelectric random access memories (FeRAM), which are intrinsically non-volatile. This application is based on the capability of ferroelectrics to switch between two opposite polarization states and to retain the polarization in the absence of an electric field [1,2].

Some advantages of BIT for use in FeRAM are its large remnant polarization, which is ~60 $\mu C\, cm^{-2}$ for the single-crystal [3] and the low processing temperature [4]. Furthermore, since the environmental considerations are becoming more and more important, it is

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considered an asset that BIT is lead-free. However, it has been found that it shows a drawback which mortgages its applicability: the amount of switched charge decreases with the number of read/write cycles (fatigue). Nevertheless, it has been shown by Park et al. [5] and Bu et al. [6] that substitution of Bi^{3+} with La^{3+} strongly improves the fatigue properties.

Lanthanum substituted bismuth titanate (BLT) has been synthesized either as a powder or a thin film by various methods (alcoholic sol–gel [7], chemical co-precipitation [8], conventional solid-state methods [9] and pulsed laser deposition [5,6]). It is generally recognized that the chemical methods, like solution–gel synthesis, enable homogeneous mixing of the cations on a molecular scale, leading to a lower formation temperature of the desired oxide phase compared to solid-state routes. In our laboratory, several multi-metal oxides have been synthesized successfully via sol(ution)–gel routes, alcoholic as well as aqueous [10–13].

Here, an aqueous solution–gel route is presented for the preparation of $Bi_{3.5}La_{0.5}Ti_3O_{12}$, a composition which was chosen because of its superior hysteresis and fatigue behavior [5,6]. Other compositions are easily accessed by the same route. The reasons for choosing an aqueous route to BLT are economics and love of ease. The metal alkoxides and alcoholic solvents used in other sol–gel techniques are expensive and the alkoxides' sensitivity towards air humidity requires the use of a nitrogen flushed glove box, which hinders carrying out the experiments. Furthermore, the alcoholic solvents contain great health risks, e.g. methoxyethanol, very commonly used, is suspected to be a teratogen.

2. Experimental

2.1. Materials and reagents

For the gel synthesis and the interpretation of the spectra the following materials were used: bismuth(III)acetate ($Bi(CH_3COO)_3$, Aldrich, >99.99%), lanthanum(III)acetate hydrate ($La(CH_3COO)_3{\cdot}xH_2O$, Alfa Aesar, 99.9%), citric acid ($C_6H_8O_7$, Aldrich, 99%), acetic acid (CH_3COOH, Acros, 99.8%), Ti(IV)-isopropoxide ($Ti(C_3H_7O)_4$, Acros, >98%), hydrogen peroxide (H_2O_2, Acros, 35 wt.% in H_2O, stabilized), ammonia (NH_3, UCB, 25 wt.% in H_2O), citraconic acid ($C_5H_6O_4$, Acros, >99%), citraconic anhydride ($C_5H_4O_3$, Acros, 98%), itaconic acid ($C_5H_6O_4$, Aldrich, >99%), itaconic anhydride ($C_5H_4O_3$, Acros, 98%) and *trans*-aconitic acid ($C_6H_6O_6$, Acros, 98%).

2.2. Gel synthesis

An aqueous 0.04 mol l^{-1} solution of bismuth acetate was prepared using 8 ml CH_3COOH per g $Bi(CH_3COO)_3$. A lanthanum acetate solution (0.01 mol l^{-1}) was prepared by drop-wise addition of acetic acid to $La(CH_3COO)_3{\cdot}xH_2O$ in H_2O. The precursor solution for Ti^{4+} (0.1 mol l^{-1}) was prepared as described elsewhere [12]. Hydrolysis of Ti(IV)-isopropoxide in H_2O leads to the precipitation of a hydroxide to which H_2O_2 and citric acid are added, both in a 2:1 molar ratio against Ti^{4+}. The pH of the resulting Ti(IV)peroxocitrato solution is adjusted to pH = 7 using NH_3. All of the metal concentrations mentioned earlier were verified by ICP-AES using a Perkin-Elmer Optima 3000 DV.

The BLT gel preparation is presented schematically in Fig. 1. When stoichiometric amounts (Bi, 3.5; La, 0.5; Ti, 3) of the three monometallic solutions are simply united, precipitation (i.e. loss of homogeneity) occurs upon drying in a furnace at 60 °C under flowing air. After testing, it became evident that the addition

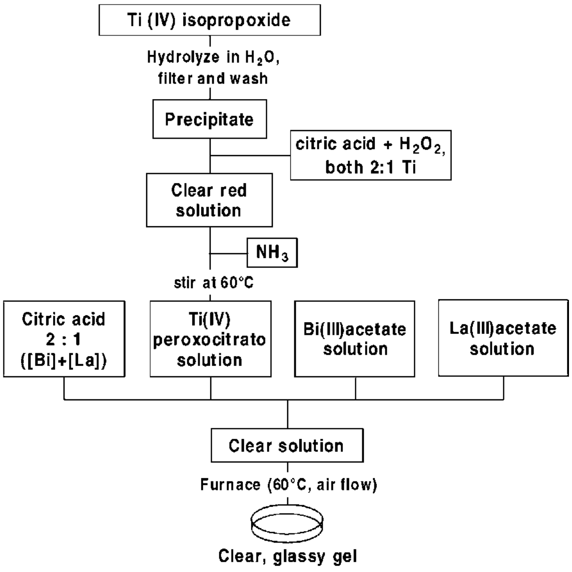

Fig. 1. Flow chart of the $(Bi,La)_4Ti_3O_{12}$ gel synthesis.

of supplementary citric acid in a molar ratio of at least 2:1 against the total of Bi^{3+} and La^{3+} is needed to obtain a clear gel. The pH of a BLT precursor solution prepared in this way is 3.5. Gelation and drying of this solution was carried out on a Petri dish, in a furnace at 60 °C under flowing air. The resulting gel was proven to be amorphous by XRD and was used for further investigation.

2.3. Characterization techniques

The thermal decomposition pathway of the BLT gel is studied by means of TGA (TA Instruments TGA 951-2000) on-line coupled to a FTIR spectrometer (Bruker IFS 48) or a quadruple mass spectrometer (MS, Thermolab VG Fisons). Both of these techniques allow analysis of the gases emitted during decomposition but here they are used in a complementary manner [14]. In TGA–FTIR, the evolving gas molecules are detected as such which facilitates their identification. However, as IR peaks often overlap it can happen that certain compounds are overlooked. In TGA–MS the evolving gas molecules are fragmented during ionization, which makes the interpretation of the spectra more difficult, yet there is a good chance of finding an ion which is not spectrally interfered and it has a lower detection limit. This is illustrated by the example of H_2O which is easily detected in TGA–MS at $m/z = 18$, but not in TGA–FTIR since it shows only broad bands between 2200–1200 and 4000–3400 cm^{-1} regions which are spectrally interfered. In order to avoid fragmentation of H_2O into OH, which would interfere with the signal of NH_3 ($m/z = 17$), the ionization energy is set to 20 eV. The MS was set to scan only the range between $m/z = 15$ and 115, as the most important ions were expected to be situated here.

The heating rate in all of the performed TGA experiments was 10 $°C\,min^{-1}$ and the gas flow was always set to 100 $ml\,min^{-1}$.

The changes occurring in the solid phase during gel decomposition are studied by means of high temperature-diffuse reflection infrared Fourier transform spectroscopy (HT-DRIFT, Bruker IFS 66). As parts of the HT-DRIFT compartment would be damaged, if heated above 400 °C in dry air, the HT-DRIFT experiment was only performed up to this temperature. In order to obtain information on the sample composition at higher temperatures, the BLT gel was heated in a TG furnace to the specified temperatures and quenched. Afterwards, DRIFT spectra were recorded at room temperature for the samples prepared in this way. In inert atmosphere, HT-DRIFT measurements were performed up to 700 °C.

XRD spectra were recorded on a Siemens D5000 X-ray diffractometer using Cu $K\alpha 1$ radiation.

3. Results and discussion

3.1. Decomposition in dry air

The TGA and DTG data, measured at a heating rate of 10 $°C\,min^{-1}$ are shown in Fig. 2. The BLT gel decomposition occurs in four steps centered at 80, 190, 340 and 455 °C. The ‘second step’ is very broad, seems to comprise two maxima indicating several overlapping processes are taking place, and also occurs in inert atmosphere (see Section 3.2). The last two steps are not seen in inert atmosphere at the exact same temperatures which leads to the conclusion that atmospheric O_2 plays a role in these steps.

3.1.1. Evolved gas analysis: TGA–MS and TGA–FTIR

In order to be able to assign certain mass fragments detected in TGA–MS, reference (TGA–)MS spectra were recorded (at 20 eV ionization energy) for acetic acid, citric acid and several known [15] decomposition intermediates of citric acid, namely, *trans*-aconitic, itaconic and citraconic acid as well as itaconic and citraconic anhydride.

Acetic acid is rather volatile, so it was possible to record a mass spectrum at room temperature by simply holding an open bottle in front of the MS-capillary. It was found that acetic acid produces ions with $m/z =$ 15, 41, 42, 43, 45, 46, 59, 60 and 61.

Citric acid and its intermediates were heated in He (100 $ml\,min^{-1}$) in the TGA at the same heating rate as the BLT gel (i.e. 10 $°C\,min^{-1}$) and simultaneously mass spectra (20 eV ionization energy) of the evolving gas molecules were recorded. These mass spectra were all very similar, which is reasonable since (partial) decomposition does take place during heating in the TGA. Citric acid and all of its investigated intermediates produced ions with m/z values of 39 (C_3H_3), 40 (C_3H_4), 41 ($^{13}C_3H_4$), 68 (C_4H_4O) and 112 ($C_5H_4O_3$,

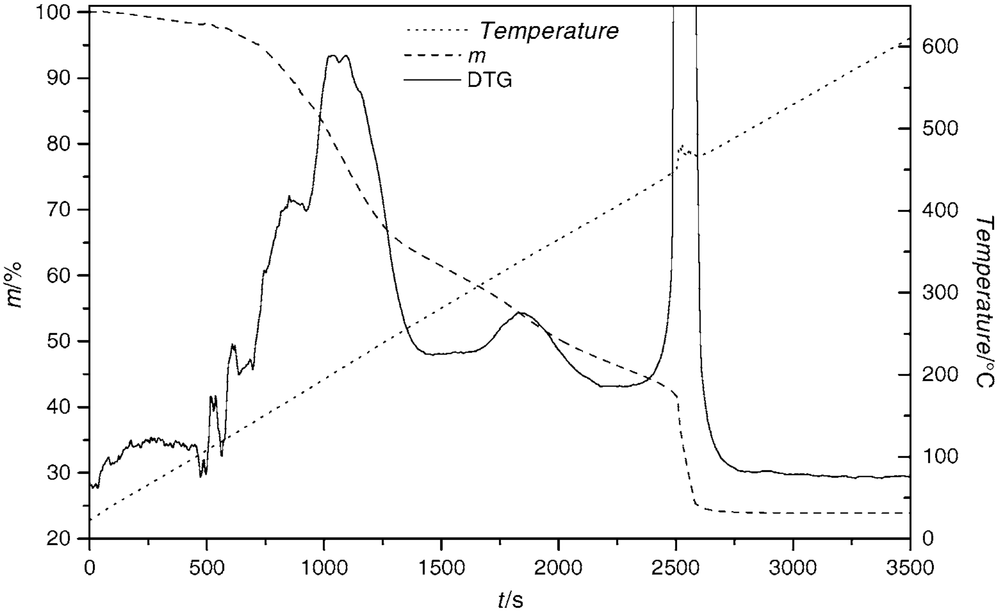

Fig. 2. TG/DTG for BLT gel in dynamic dry air (10 °C min^{-1}).

itaconic or citraconic anhydride), of which 39 and 68 were among the most intense. All of the investigated carboxylic acid intermediates showed ions with $m/z =$ 18, 44 and 45, while $m/z = 43$ was seen for all except for citraconic acid. Two conclusions can be drawn from these experiments: the ions with $m/z = 39$ and 68 can be considered as indications for the decomposition of citric acid and it is impossible to distinguish between citric acid and its intermediates by means of TGA–MS (at least at 10 °C min^{-1}).

In TGA–FTIR of acetate-containing gels the identification of these acid and cyclic anhydride intermediates is practically impossible because of the interference with acetic acid vibrations taking up the entire region between 960 and 1400 cm^{-1} and with its C=O stretch, located at 1785 cm^{-1}.

The gases evolved during the four steps of the BLT gel decomposition were analyzed by means of FTIR and MS. The assignment of the most important mass fragments and IR bands is summarized in Table 1, together with the temperatures at which the concerned compounds peak. A selection of certain ion abundance and integrated absorption of characteristic IR vibrations is shown as a function of time in Figs. 3 and 4, respectively. The TGA–FTIR integration were calculated for the following wavenumber intervals: 2268–2395 cm^{-1} (asymmetric C=O stretching of CO_2), 2217–2137 cm^{-1} (carbon monoxide stretch), 1840–1723 cm^{-1} (carbonyl stretch of acetic acid) and 940–913 cm^{-1} (NH_3 rocking).

Water ($m/z = 18$) is seen very early at 80 °C. This is due to residual solvent evaporating from the sample. When looking at the temperature range around 200 °C, which is, here, called ‘the second step’, it becomes clear that during this step several processes are taking place. Around 150 °C the first peak for ammonia is seen in TGA–MS as well as in TGA–FTIR. This can be ascribed to the decomposition of ammonium citrate and acetate, formed from the ammonia present in the Ti^{4+} solution and the excess of citric acid or the acetic acid in the Bi^{3+} and La^{3+} solutions. The developed ammonia is liberated immediately, followed directly by acetic acid (Figs. 3 and 4). In Fig. 3, acetic acid is represented by $m/z = 60$, but other fragments (15, 41, 42, 43, 45, 46, 59, 60 and 61) were also detected and assigned to acetic acid at this temperature. No acetic acid evolves after 230 °C, which may indicate that the acetate groups were not or only very loosely coordinated to the metal ions. Note that acetic acid is detected in TGA–FTIR up to 320 °C during the decomposition of bismuth acetate and around 370 °C for lanthanum acetate. At 205 °C

Table 1
Peak assignment and occurrence of mass fragments/IR bands in TGA–MS/TGA–FTIR of the BLT gel in dry air and inert atmosphere

m/*z*	Fragment(s)	Peaks in dry air at temperature (°C)	Peaks in He at temperature (°C)
TGA–MS			
15	CH_3	185, 340, 455	180, 330, 430
17	NH_3	150, 240, 455	200 (broad), 440
18	H_2O	80, 205, 340, 455	80, 220, 330
30	NO	455	195, >480
39	C_3H_3[a]	205	210, 255
41	Fragment of CH_3COOH, $^{13}C_3H_4$[a], C_2H_3N	185, 290, 340, 455	185, 295, 345, 410
42	CH_2CO	185	180
43	CH_3CO	185, 340, 455	180, 350
44	CO_2	225, 340, 455	> 200
45	$^{12}COOH$	185, 340, 455	180
46	NO_2, $^{13}COOH$[a], (CH_3COOH)	185, 340, 455	180
60	CH_3COOH	185	180
68	C_4H_4O[a]	205, 250	210, 255
111	3-Methyl-maleimide $C_5H_5NO_2$	215, 255	215, 255
Wavenumber (cm^{-1})	Assigned to	Peaks in dry air at temperature (°C)	Peaks in Ar at temperature (°C)
TGA–FTIR			
667, 2330, 3615, 3715	CO_2	225, 340, 455	225, 320, 420, 590, 870
2110, 2180	CO	340, 455	>720
930, 964, 1623, 3330	NH_3	150, 240, 455	150, 230, 440, 585
995, 1070, 1180, 1270, 1390, 1785, 3580	CH_3COOH	185	185

[a] Fragments from (decomposition products of) citric acid.

water is liberated together with mass fragments 39 ($C_3H_3^+$) and 68 ($C_4H_4O^+$, Fig. 3), which show the same profile versus time. From this it can be concluded that by 205 °C citric acid, formed from ammonium citrate, has started to decompose, with dehydration into aconitic acid as a first step. At 225 °C, the first peak in the profile of CO_2 (Figs. 3 and 4) is detected, but its liberation had already started around 190 °C. This is not a combustion, as it is also seen in inert atmosphere (see Section 3.2.1), but it is due to decarboxylation reactions converting aconitic acid into itaconic acid, which can dehydrate into the cyclic itaconic anhydride. In summary, it can be said that between 200 and 275 °C, free citric acid decomposes yielding H_2O, CO_2 and several other decomposition products. The ion with $m/z = 111$, seen around 235 °C (Fig. 3), is no fragment of the mentioned decomposition products of citric acid. This ion might be 3-methyl-maleimide ($C_5H_5NO_2$), a cyclic imide similar to citraconic anhydride. It may result from a nucleophilic reaction of NH_3 on an acid group of, e.g. itaconic acid, leading to the formation of an amide and subsequent intramolecular dehydration followed by an isomerization, analogous to the one from itaconic to citraconic anhydride, would then yield 3-methyl-maleimide [16]. The formation of these amides during the evolution of ammonia around 150 °C also holds an explanation for the appearance of a second ammonia peak around 240°C, because it is possible that the newly formed amides are partially hydrolyzed by the evolving water. Around 290 °C a maximum for a fragment with $m/z = 41$ appears. The same phenomenon is observed when an ammonium citrate gel, prepared by evaporation of a citric acid solution after raising its pH to 3.5 with NH_3, is heated at 10 °C min^{-1} in dry air. The odd mass indicates that this fragment contains an odd number of nitrogens (nitrogen rule [17]), so it may be C_2H_3N originating from a decomposing or evaporating nitrile, formed from the amides.

Around 340 °C, the third step takes place in the decomposition pathway of the BLT gel. The fragments and compounds detected in TGA–MS

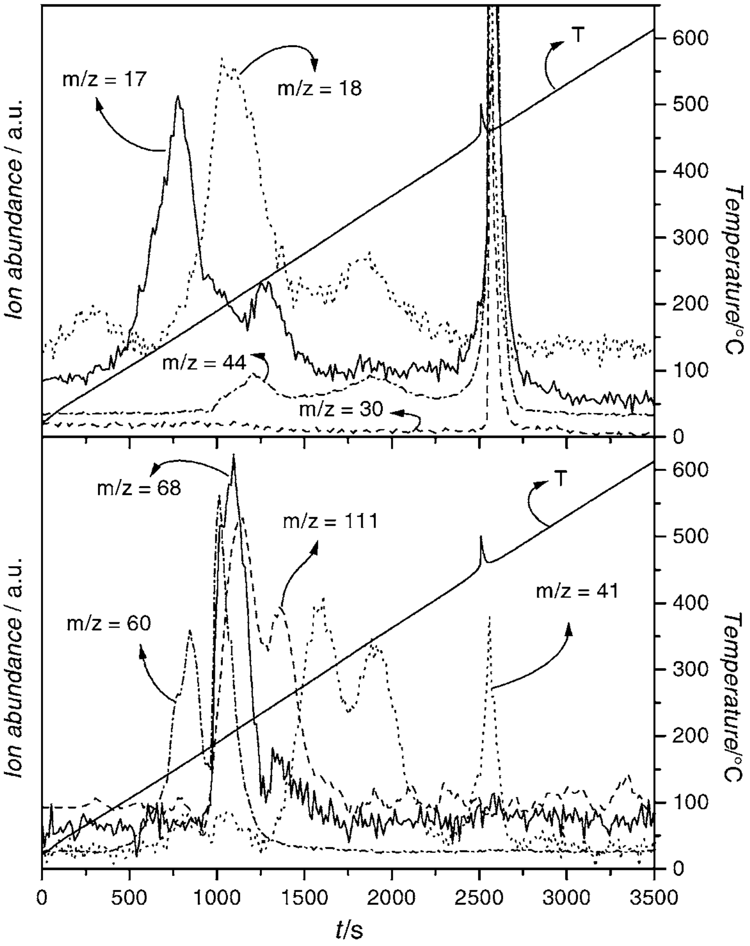

Fig. 3. TGA–MS for BLT gel in dynamic dry air.

and/or TGA–FTIR are CH_3^+, $^{13}C_3H_4^+$ or $C_2H_3N^+$, CH_3CO^+, $COOH^+$ or $^{13}CO_2^+$, H_2O^+, CO and CO_2. These fragments prove that there still exist organic compounds which are combusted or undergo decarboxylation and dehydration at 340 °C, contrasting with all of the reference acids and anhydrides which already decompose at temperatures below 250 °C. It can be concluded that during the third step, citrate ligands coordinating the metal ions are decomposed. Furthermore, this de-coordination and subsequent formation of metal oxide bonds are supported by the HT-DRIFT measurements discussed in Section 3.1.2.

The final step occurs around 455 °C. In TGA–MS a strong decrease of the signal at $m/z = 32$ (O_2) below the background level of dry air (ca. 20% O_2) is observed, indicating that oxygen is consumed. Because of the resulting temporary lack of oxygen, compounds such as NH_3, NO, CO and organic products ($^{13}C_3H_4^+$or $C_2H_3N^+$, CH_3^+, CH_3CO^+, $COOH^+$ or $^{13}CO_2^+$) are liberated, together with the more ordinary combustion products CO_2, H_2O and NO_2. This step is ascribed to the combustion of any organic material left in the gel. The nitrogen containing compounds would be brought forth by amides present in the gel, formed as described.

3.1.2. The solid phase: HT-DRIFT

The HT-DRIFT spectra for the BLT gel are shown in Fig. 5. The region around 3000 cm^{-1}

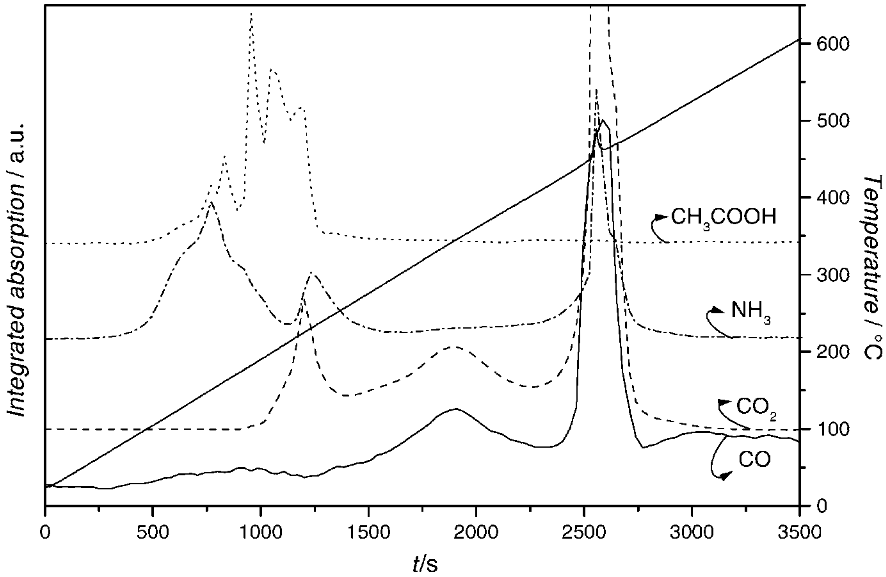

Fig. 4. TGA–FTIR for BLT gel in dynamic dry air.

shows one extremely broad band, which is ascribed to the O–H stretches of the residual H_2O solvent molecules (around 3500 cm^{-1}), to the ammonium groups (3300–3030 cm^{-1}) and the O–H stretches of carboxylic acids (3000–2500 cm^{-1}). Of course the C–H stretches of the citrates and acetates are also situated here (around 2900 cm^{-1}). A second important region is the one between 1830 and 1500 cm^{-1} where C=O stretching bands of e.g. carboxylic acids and acid anhydrides can be found, as well as amide I

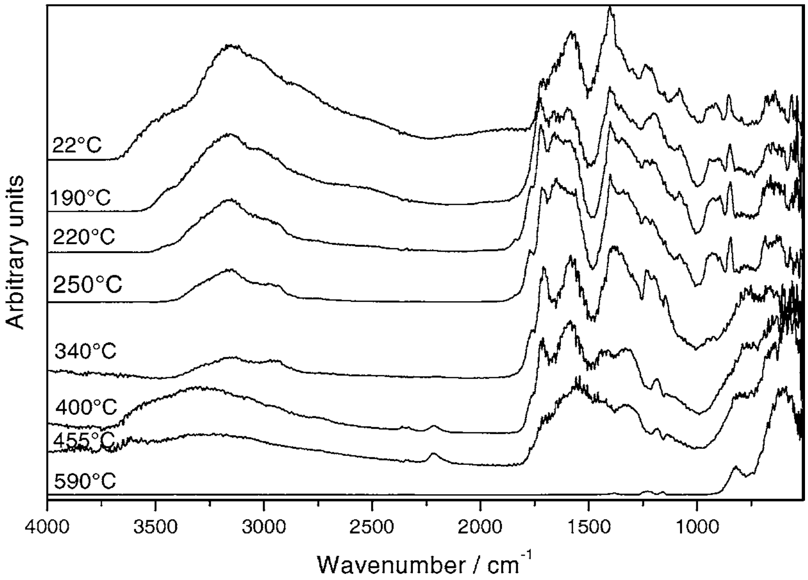

Fig. 5. HT-DRIFT spectra for BLT gel in dynamic dry air.

and II bands at elevated temperatures. The bands at 1575 and 1400 cm^{-1} are ascribed to the carboxylate functions of acetate and citrate ions bound to ammonium groups or coordinated to metal ions. The band at 1080 cm^{-1} is ascribed to the C–O (–H or –metal) stretch. The bands at 926, 853 and 650 cm^{-1} are ascribed to peroxo groups and bonds involving metal atoms [18].

At 190 °C, the drying of the sample and the disappearance of ammonia is evident from the diminishing of the band around 3500 cm^{-1}. The subsequent formation of free acid functions is seen from 190 °C onwards by the increasing intensity of the C=O stretch at 1720 cm^{-1}. From 220 to 250 °C, two small peaks at 1765 and 1840 cm^{-1} are seen. These peaks are ascribed to (cyclic) anhydrides (e.g. itaconic anhydride, which isomerizes into citraconic anhydride) formed from the decomposing citric acid.

The band at 1080 cm^{-1} ($\nu_{C–O}$) disappears in the course of the third decomposition step and the carboxylate bands at 1575 and 1400 cm^{-1} also diminish from 340 °C onwards. These are indications for the decomposition of the citrate ligands on the metal ions. In the region below 1000 cm^{-1} M–O bands are appearing, which become stronger around 400 °C.

The band around 2215 cm^{-1} in the spectra at 400 and 455 °C is ascribed to adsorbed carbon monoxide [16] which is liberated in this temperature interval (see Fig. 4). During the step at 455 °C, all of the residual organic matter is removed as seen in the spectrum taken at 590 °C. There are two bands at 820 and 590 cm^{-1} which can be ascribed to Ti–O stretches in octahedral TiO_6 groups, in accordance with BIT bands at 810 and 580 cm^{-1} [19].

An XRD spectrum taken for the BLT, after heating in dry air at 10 °C min^{-1} up to 800 °C with an isothermal period of 15 min in a TG furnace showed only peaks at the same positions as for BIT (JCPDS 35-0795 [20]) which confirms that the substitution of La^{3+} for Bi^{3+} was successful. Optimization of the heat treatment will be the subject of future work.

3.2. Decomposition in inert atmosphere

The TG and DTG of the BLT gel in inert atmosphere (either argon or helium) at a heating rate of 10 °C min^{-1} are shown in Fig. 6. The decomposition in inert atmosphere seems to comprise six steps centered at 70, 200, 330, 420, 590 and 910 °C, respectively, but they are not well defined. Since the decomposition takes place very gradually, the mechanism is more difficult to describe than in dry air.

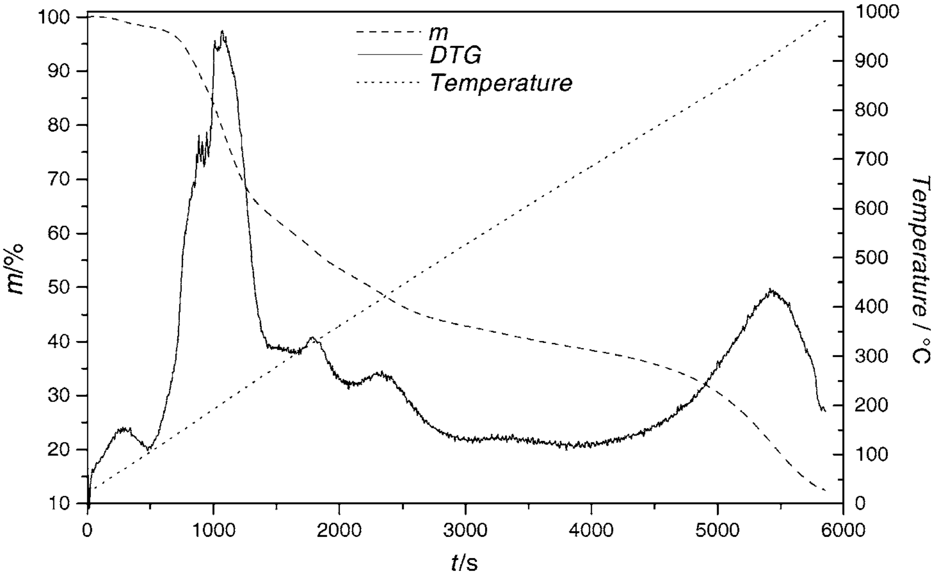

Fig. 6. TG/DTG for BLT gel in dynamic argon (10 °C min^{-1}).

3.2.1. Evolved gas analysis: TGA–MS and TGA–FTIR

A summary of the results from TGA–MS and TGA–FTIR in He and Ar, respectively, is shown in Table 1 and Figs. 7 and 8. The first three steps are similar to the decomposition in dry air. Residual water ($m/z = 18$) is removed from the gel around 70 °C. Between 100 and 300 °C, a great many fragments and compounds are detected. From TGA–FTIR, it is clearly seen that ammonia ($m/z = 17$) is liberated in two steps: in the first step, it is followed immediately by acetic acid ($m/z = 15$, 41, 42, 43, 45, 46, 59, 60 and 61) and in the second, it is followed by several fragments of (decomposition products of) citric acid (H_2O, CO_2, $C_3H_3^+$, $^{13}C_3H_4^+$ and $C_4H_4O^+$) and by 3-methyl-maleimide. It is clear that ammonium acetate decomposes first, followed by ammonium citrate. Between 305 and 355 °C, CO_2, H_2O, $^{13}C_3H_4^+$ or $C_2H_3N^+$, CH_3^+, and CH_3CO^+ are detected due to the decomposition of the citrate ligands. Because of the absence of oxygen these ligands are not burnt away instantly after their release from the metal ions.

The subsequent steps differ from the decomposition in dry air. Around 420 °C, CO_2, NH_3, CH_3^+, and $^{13}C_3H_4^+$ or $C_2H_3N^+$ are detected, which is very similar to the results of a TGA–MS measurement on the ammonium citrate gel mentioned earlier. Ammonia is also seen at higher temperatures (Fig. 8) which can be explained by the decomposition of amides or nitriles. At very high temperatures (above 750 °C) an increase

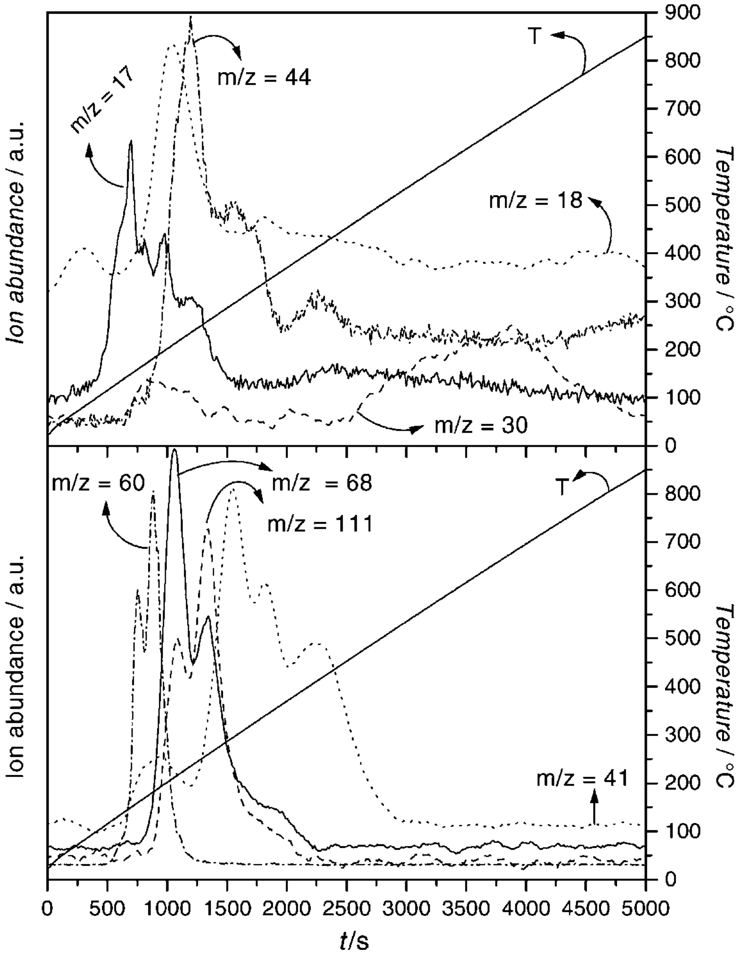

Fig. 7. TGA–MS for BLT gel in dynamic He.

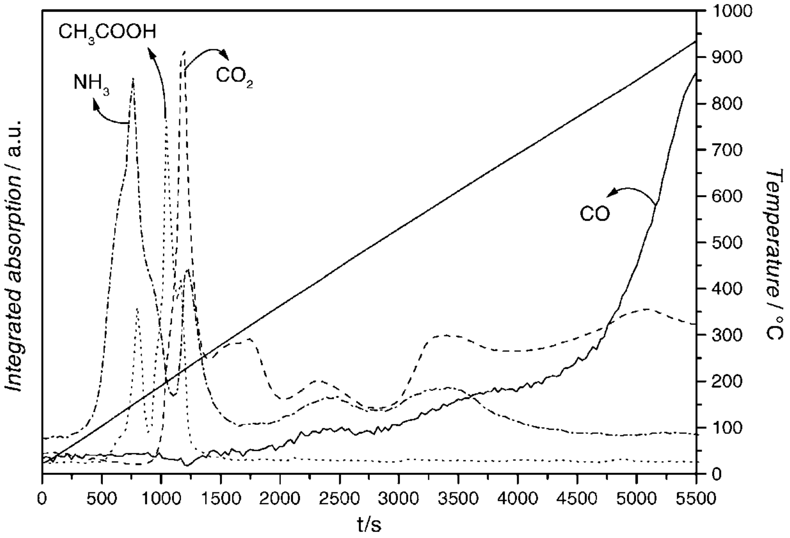

Fig. 8. TGA–FTIR for BLT gel in dynamic argon.

of the CO signal (Fig. 8) is detected. It can be concluded that above 400 °C a slow and gradual decomposition of (nitrogen-containing) residual organic matter takes place, which is not completed until 1000 °C.

3.2.2. *The solid phase: HT-DRIFT*

Between room temperature and 200 °C (Fig. 9), the drying of the sample and the disappearance of ammonia is seen again and from 220 to 250 °C the cyclic anhydrides are detected. The band at 1080 cm^{-1} ($\nu_{C\text{–}O}$) disappears in the course of the third decomposition step around 330 °C but the carboxylate C=O stretches at 1575 and 1400 cm^{-1} still remain. Above 400 °C, these bands clearly show a lower intensity, which is in accordance with the suggested gradual decomposition of organic residue. No oxide bands appear below

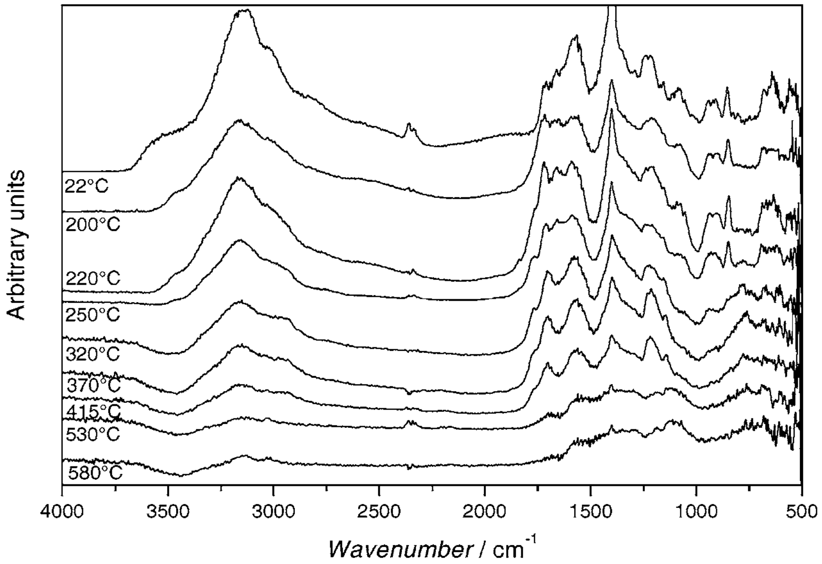

Fig. 9. HT-DRIFT spectra for BLT gel in dynamic argon.

750 cm^{-1} at any temperature up to 700 °C. If the gel is heated further to 1000 °C and kept at this temperature for half an hour, the residue is white and has a DRIFT spectrum showing only one broad band centered at 595 cm^{-1}, indicating that there are no organic compounds left.

4. Conclusion

An aqueous metal–chelate $Bi_{3.5}La_{0.5}Ti_3O_{12}$ gel was thermally decomposed in dry air and in inert atmosphere. Based on the on-line analyses of the evolved gases and of the solids, a scheme for the decomposition mechanism has been proposed.

In dry air it consists of four steps. After evaporation of the remainder of the solvent, ammonium acetate and citrate are decomposed. If there are any metal acetates present in the gel, they are also decomposed in this second step. The third step comprises the decomposition of citrate ligands coordinated to the metal ions, giving rise to the formation of metal oxide bonds. The last step consists of the combustion of all residual organic matter including amides formed during the decomposition process. In the last two steps, oxygen gas plays an important role. Decomposition of the gel in dry air leads to the formation of a powder with the desired crystal structure. Spin- or dip-coating of the aqueous precursor solution followed by thermal decomposition will allow deposition of thin films for application in FeRAM.

The absence of O_2 leads to a change in the decomposition pattern of the gel. In the low temperature region, the decomposition runs parallel to the one in dry air, but starting from approximately 400 °C the decomposition pathways diverge. It has turned out to be impossible to remove all organic matter from the gel at economically feasible temperatures.

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