Thermal decomposition of lanthanum-titanium citric complexes prepared from ethylene glycol medium

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The paper addresses the thermal decomposition of La-, Ti- and bimetallic La-Ti-non-crystalline citric complexes, prepared in ethylene glycol medium. The latter complex is the starting material for the effective ferroelectric $La_2Ti_2O_7$ preparation by the polymerized complex method. Based on thermogravimetric analysis (DTG, DTA and TG) and identification of some of the intermediates (by elemental analysis, NMR and IR spectroscopy and X-ray diffractometry), it is established that the thermal destruction proceeds step-wise, starting with dehydration above 50–60°C, partial transformation of the citrate to aconitate up to 200°C, followed by releasing of the ethylene glycol bonded as adduct and ester (200–280°C) and decarboxilation (280–335°C). The complete destruction of the organic components results in mixed-metal oxocarbonate. The process is completed at ~750°C giving poorly crystalline $La_2Ti_2O_7$. The results obtained are compared with those for a water-prepared NH_4-La-Ti-citric complex. © *2002 Kluwer Academic Publishers*

1. Introduction

The polymerized complex method (PCM), a version of the sol-gel technology, is a convenient method for a preparation of multicomponent compounds with good stoichiometry, phase homogeneity, and perfect crystal structure. The method is based on the formation of polymeric resin as a result of polyesterification of metal complex(es) of a hydroxocarboxilic acid (most often citric, CA) with a polyvalent alcohol (ethylene glycol, EG). Upon heating, the desired product of the metals used is obtained at relatively low temperatures.

Obviously, knowledge of the chemical nature of the three main processes involved in PCM (complexation, esterification/polyesterifacation, and thermal decomposition), is of great significance for the optimal application of the method. Indeed, a number of papers [1–15], dealing mainly with the synthetic aspects of the method, report more or less detailed data concerning the thermochemical behavior of the polymer resin-precursors to formation of the final compounds.

According to published reports [3, 6, 10], the bimetallic citric complexes formed in the initial EG solution remain stable during heat treatment up to the formation of the black amorphous precursors at 400–500°C. Contrary to these findings, Cho *et al.* [2] maintain that the type of coordination of CA acid groups to Sr and Ti ions changes with the temperature increase: unidentate in the initial solution, bridging in the polyester resin and ionic in the amorphous precursor. Further heating of the amorphous precursor leads to multicomponent oxide formation as a result of organic component burning.

Due to the rather complicated nature of the real systems (solutions with a great excess of CA and EG, or polymer resins, respectively), more precise and detailed data on the complexation and on the thermal decomposition can be expected studying the complexes isolated from the initial solutions.

Similar investigations have been carried out about a few complexes; those were prepared, however, in aqueous solutions. Henings and Mayr [16] proposed a scheme of the thermal decomposition of Ba-Ti-citrate. The established transformation of the citrate to aconitate (as a result of an intramolecular dehydration) is confirmed for Li-Co-, NH_4-Li-Co- [17] and Li-Ni- [18] citrates. Some authors [3, 5, 6] challenge Henings and Mayr's conclusion that the mixed-metal complex is decomposed to $BaCO_3$ and TiO_2, and that $BaTiO_3$ formation is the result of the following solid state reaction enhanced by the high dispersion and intimate mixing of the compounds. They found evidence for the formation of mixed-metal oxocarbonate, decomposing directly to dititanate.

$Ln_2Ti_2O_7$, effective ferroelectrics (Ln = La, Nd) or ionic conductor (Ln = Y), were also prepared by the PCM, and some results of a thermogravimetric study of the polymer resin, formed in the system La^{3+}-Ti^{4+}-CA-EG, have been reported in [7, 8]. The thermal decomposition of the respective amorphous precursors is found to be a two-stage exothermic process. The higher exothermic event at ~470°C is attributed to burnout of most of the organic components involved in the precursor. According to the authors the much weaker exothermic event around 800°C, which corresponds to a small

weight loss, can be attributed either to the completion of burnout of residual carbonates in the decomposition product after the first exotherm, or to the onset of crystallization to $Ln_2Ti_2O_7$.

Using the above-mentioned approach (examination of isolated complexes), we studied the composition and some spectral characteristics of the solid La-Ti-citric complexes isolated from the initial EG-solution [19]. The present paper presents the results from the study of the thermal decomposition of this complex, as well as that of the monometallic La- and Ti-citrates, prepared under the same conditions.

2. Experimental
2.1. Synthesis of the complexes

$La(NO_3)_3 \cdot 6H_2O$, anhydrous citric acid and Ti-tetraisopropylate $Ti/OHC(CH_3)_2/_4$ (Merck), ethylene glycol, p.a. (Poch, Poland), acetone, p.a. and 25% ammonia solution, p.a. were used for the preparation of the complexes both in ethylene glycol and in water media.

The synthetic methods described earlier [19] were used; the ethylene glycol solutions were heated at 120°C for 30 min. The experiment in the latter medium were carried out under conditions as close as possible to the ones for the PCM [7]. Mole ratios $La^{3+} : Ti^{4+} : CA : EG = 1 : 1 : 10 : 40$, $La^{3+} : CA : EG = 2.3 : 10 : 40$ and $Ti^{4+} : CA : EG = 1.7 : 10 : 40$ were adjusted in the initial solutions for the preparation of the respective bimetallic and monometallic products. Acetone was used to desalt the complexes obtained in both media. Traces of adsorbed EG were found in products isolated from the EG solution. They were removed keeping the complexes in acetone for 24 h. The samples were dried in air and stored in tightly closed vessels without any change in the composition for an extended period of time.

2.2. Analysis

DTA, DTG and TG curves of ~0.2 g samples were recorded by a Paulik-Paulik-Erdey derivatograph (MOM, Hungary) in a synthetic corundum crucible in static air heated up to 1000°C (10°C/min); sensitivity: TG-200 mg, DTA-1/5, DTG-1/10. Al_2O_3 was used as a standard. The calibration for TG and DTA was made using $CaC_2O_4 . 2H_2O$. Samples were also heated to interstitial temperatures in order to identify some of the intermediates. The reproducibility of the results for different batch samples was very good even when slight variations in the synthetic procedure were allowed. Naturally, significant quantitative differences in the curve patterns were observed when different heating times were applied to the initial solutions, mainly due to the increase of the esterification degree of the ligands. Differential scanning calorimetry (DSC) was carried out up to 300°C using Perkin-Elmer DSC-2C in air.

The H, C and N contents in the separated products and in some intermediates were determined by the common organic analysis methods, and the content of La and Ti by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The analytical lines—408.672 nm

(La) and 323.657 nm (Ti)—were isolated on the basis of earlier results [20, 21]. The determination of the metals was performed in solutions that were obtained by melting ~0.5 g of the sample with ~10 g of $KHSO_4$ and dissolving the melt in H_2SO_4 (5%). IR-spectra (4000–400 cm^{-1}, KBr-pellets) were recorded using a FT spectrometer Bomem Michelson 100 or Specord 75 (C. Zeiss, Germany). ^{13}C- and ^1H-NMR spectra at room temperature were taken using a Bruker-250 MHz spectrometer with D_2O as a solvent. X-ray powder diffractograms were recorded using a TUR-M62 (Germany) diffractometer with Co K_α radiation at 30 kV and 20 mA at a scan rate of θ 0.03°/2 s.

3. Results and discussion

The compositions of the complexes studied are shown in Table I. The contents of the water and the residue after ignition are determined from the TG-data discussed below. The relative content of EG- bonded as an adduct or an ester is derived from ^1H-NMR spectra. The shift at 91 ppm in ^{13}C-NMR spectra is indicative of the presence of ligands with deprotonated alcoholic OH groups of the CA. The summary of the interpretation of the NMR spectra is given in [19, 22]. The reported results along with the IR data allow the complexes' composition to be described by the formulae that are presented in Table II, supposing [23] mixed-metal complexes formation in the bimetallic systems. The agreement between the experimentally observed data and those calculated according to the proposed formulae is in most cases within the range of ±5%.

The DTG, DTA and TG curves of the studied La-, Ti- and La-Ti-citrates, prepared in EG medium, as well as those of the analogous La-Ti-(actually, the NH_4-La-Ti-) complex, prepared in water solution, are shown on Figs 1–4. Table III summarizes some of the parameters for the processes, and presents the possibility of comparing the experimentally observed mass losses in the different stages with the one that was calculated on
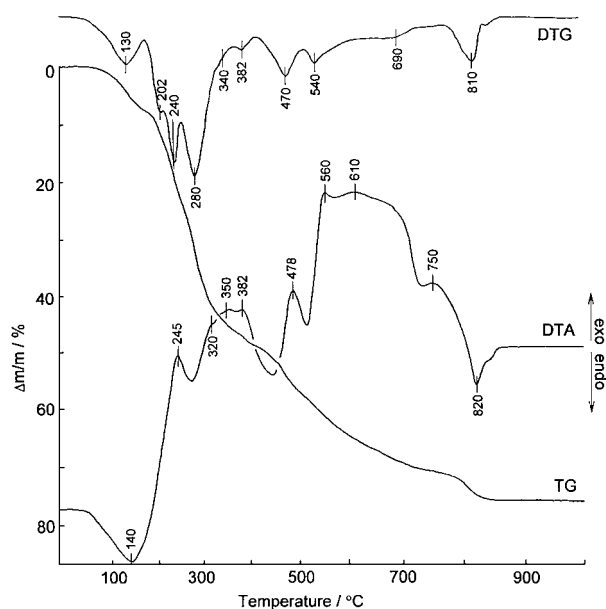
Figure 1 DTG, DTA and TG curves of the La-citrate prepared in EG medium (LaC120).

TABLE I Composition of the studied complexes

Sample symbol[a]	H		C		N		La		Ti		H2O		Residue[b]		Mole ratio according to NMR-data						Shift at 91 ppm in 13C-NMR spectra
															HOROH/Cit[c]		ROH/Cit[c]		R/Cit[c]		
	F[d]	C[d]	F	C	F	C	F	C	F	C	F	C	F	C	F	C	F	C	F	C	
LaC120[e]	4.19	3.90	26.58	27.96	–	–	23.03	23.78	–	–	9.0	9.2	25.3	27.9	0.10	0.06	0.83	0.65	0.33	0.29	No
TiC120[e]	5.21	5.60	34.44	35.62	–	–	–	–	6.73	6.07	9.2	9.1	11.9	10.1	0.90	0.87	0.84	0.83	0.46	0.39	Yes
LaTiC120[e]	4.54	4.40	34.04	33.87	–	–	10.44	10.94	3.56	3.77	7.1	7.1	18.3	19.1	0.10	0.10	0.84	0.88	0.52	0.50	Yes
LaTiC40w[f]	4.70	4.96	23.00	22.75	5.72	5.68	12.08	12.53	4.10	4.32	16.1	16.2	21.5	21.9	–	–	–	–	–	–	Yes

[a]See Table II.
[b]After ignition to 1000°C, calculated values are obtained supposing La_2O_3, TiO_2 and $La_2Ti_2O_7$ resp., as final products.
[c]R = CH_2CH_2, Cit = citric ligands.
[d]F-experimentally found, C-calculated according to the formula proposed in Table II.
[e]Prepared in EG medium.
[f]Prepared in water medium.

TABLE II Proposed formula of the isolated products

Sample symbol	Formula proposed[a]
LaC120	La(HCit^{3-})$_{0.1}$(HCitROH^{2-})$_{0.6}$(HCitROHRHCit^{3-})$_{0.5}$ · 0.1HOROH · 3H$_2$O
TiC120	Ti(HCitROH^{2-})$_{0.3}$(HCitROHRHCit^{3-})$_{0.6}$(Cit/ROH$_2^{2-}$)$_{0.2}$ (/CitROH/$_2$R^{4-})$_{0.3}$ · 2HOROH · 4H$_2$O
LaTiC120	LaTi(HCit/ROH/$_2$RCitRHCit^{4-})$_{0.5}$(HCit/ROH/$_2$RCitRCitROH^{4-})$_{0.5}$(CitROH^{3-}) · 0.4HOROH · 5H$_2$O
LaTiC40w	(NH$_4$)$_{4.5}$LaTi(HCit^{3-})$_{2.5}$(Cit^{4-}) · 10H$_2$O

[a]HCit = CH$_2$COOC(OH)COOCH$_2$COO; Cit = CH$_2$COOC(O)COOCH$_2$COO; R = CH$_2$CH$_2$.
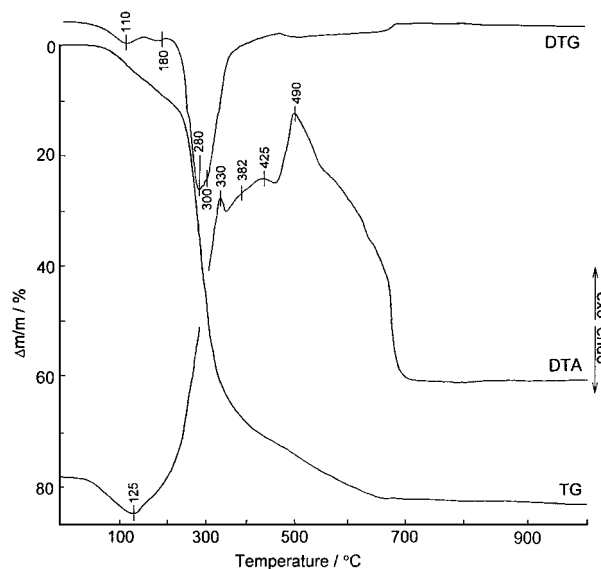

Figure 2 DTG, DTA and TG curves of the Ti-citrate prepared in EG medium (TiC120).
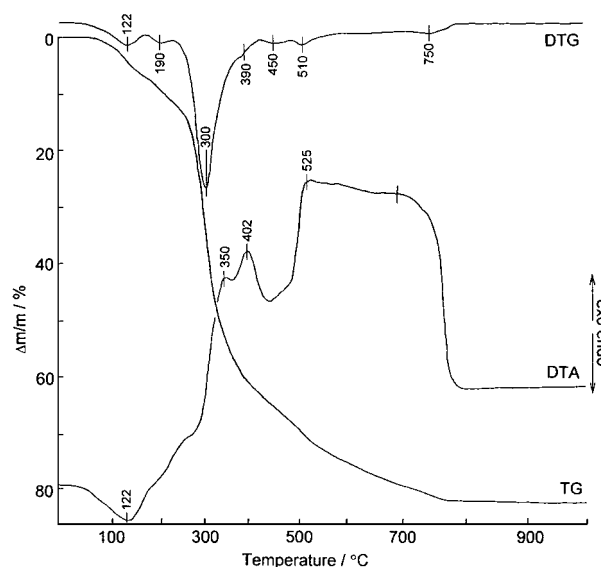

Figure 3 DTG, DTA and TG curves of the La-Ti prepared in EG medium (LaTiC120).

Figure 4 DTG, DTA and TG curves of the NH$_4$-La-Ti, prepared in H$_2$O medium (LaTiC40w); sensitivity: TG-500 mg.

the basis of the proposed hypothetical schemes for the processes (shown for La-Ti-citrates in Figs 5 and 6).

The individual La-, Ti- and the bimetallic complexes are *stable* up to 50–60°C. The *dehydration* (stages I in the Figs 1–7 and Table III) proceeds in two steps suggesting differences in the bonding mode for the water molecules present. DSC-study of the LaTiC120 (see Fig. 7) shows an endothermic event of ~53 kJ/mol H$_2$O. The two stages of dehydration in a similar temperature interval had been established for Ba-Ti-citrate obtained

from water solution [16]. That complex contains 6 mol H$_2$O/mol, and the last two of them dissociate at 150–200°C.

The *dehydration* continues as an *intramolecular* process (stage II), found also at 210°C for Ba-Ti-water prepared citrate [16], with the formation of double C=C bond (i.e., with a partial transformation of the citrate to aconitate). The process is better distinguished on DTG curves for monometallic La-citrate (see Fig. 1) and La-Ti-citrate, obtained in water (see Fig. 4), i.e., in products with higher portion of ligands with protonated alcoholic OH groups that are able to take part in this process. The analogous transformation is reported for NH$_4$-Li-Co- and Li-Co-(at 200–230°C) [17] water prepared citrates. An endothermic event is found to accompany the process for the latter compound. Such an event is seen in the case of the NH$_4$-La-Ti-product (see Fig. 4) and in the DSC-curve of the La-Ti-citrate, obtained in EG (see Fig. 7, 170–200°C). In the DTA-curves of the EG-containing products (see Figs 1–3) the endoeffect is not observed because it is masked by the stronger exoeffects of the following stages of the process.

The formation of C=C bond is confirmed by the absorption maximum at 937 cm^{-1} in the IR-spectrum of the La-Ti-intermediate (see Fig. 8), as well as by the shifts at 133 ppm in ^{13}C-and at ~5 ppm in ^{1}H- NMR spectra (see Fig. 9).

Above 200°C *the release of bonded EG as an adduct* takes place (See stage IIIa, Fig. 3). For the monometallic complexes (see Figs 1 and 2) the process can not be distinguished from the ones following it. The separation of the EG in the cited temperature range is confirmed by the disappearance of the typical band of the antisymmetrical C-O stretching vibration in EG at 1040 cm^{-1} [24] in the IR-spectrum of the La-Ti-citrate that was

TABLE III Thermal decomposition of the studied complexes

Sample symbol[a]	Parameters	I a	I b	II	III a	III b	IIIc + IV	V a	V b	VI	VII	Total
LaC120	Temperature interval (°C)	65–150	150–187	187–213		213–250	250–320	320–450	450–515	515–750	750–850	65–1000
	DTG-peak (°C)	130		202		240	280	340, 382	470	540, 630	810	
	DTA-peak[b] (°C)	140(−)		245(+)		245(+)	320(+)	350(+), 382(+)	470(+)	560(+), 610(+), 750(+)	820(−)	
	Δm/m (%)											
	F[c]	6.7	2.3	5.0		9.6	18.2	10.0	6.4	11.5	5.0	74.7
	C[c]	6.2	3.1	5.2		9.4	18.0	10.5	5.4	10.5	3.8	72.1
TiC120	Temperature interval (°C)	50–150	150–187	187–208		208–350		350–455		455–900		50–1000
	DTG-peak (°C)	110	180			280, 306						
	DTA-peak[b] (°C)	120(−)				330(+)			425(+)	490(+)		
	Δm/m (%)											
	F[c]	6.4	2.8	2.8		51.0			11.4	13.7		88.1
	C[c]	6.8	2.3	3.4		50.0			12.0	15.4		89.9
LaTiC120	Temperature interval (°C)	50–142	142–170	170–200	200–235	235–280	280–370	370–485	485–535	535–815		50–1000
	DTG-peak (°C)	122		190			300	390, 450	510	750		
	DTA-peak[b] (°C)	122(−)					350(+)	402(+)	524(+)	700(+)		
	Δm/m (%)											
	F[c]	5.8	1.3	2.3	2.0	12.3	33.4	10.0	3.5	11.1		81.7
	C[c]	5.7	1.4	2.1	1.9	12.2	33.4	9.9	3.2	11.1		80.9
LaTiC40w	Temperature interval (°C)	60–140	140–205	205–220		220–250	250–345	345–390	390–495	495–740	740–820	60–099
	DTG-peak (°C)	115	210	210		240		370	495		750	
	DTA-peak[b] (°C)	120(−)				240(−)		380(+)		480(+)		
	Δm/m (%)											
	F[c]	10.7	5.4	4.5		7.1	15.3	6.1	15.5	10.1	3.8	78.5
	C[c]	10.7	5.5	4.1		6.9	15.6	6.0	15.2	10.2	3.9	78.1

[a] See Table II.

[b] (−)-endo, (+)-exoeffect.

[c] Δm/m-relative mass loss; F-experimentally found, C-calculated according to the respective schemes (Figs 5 and 6).
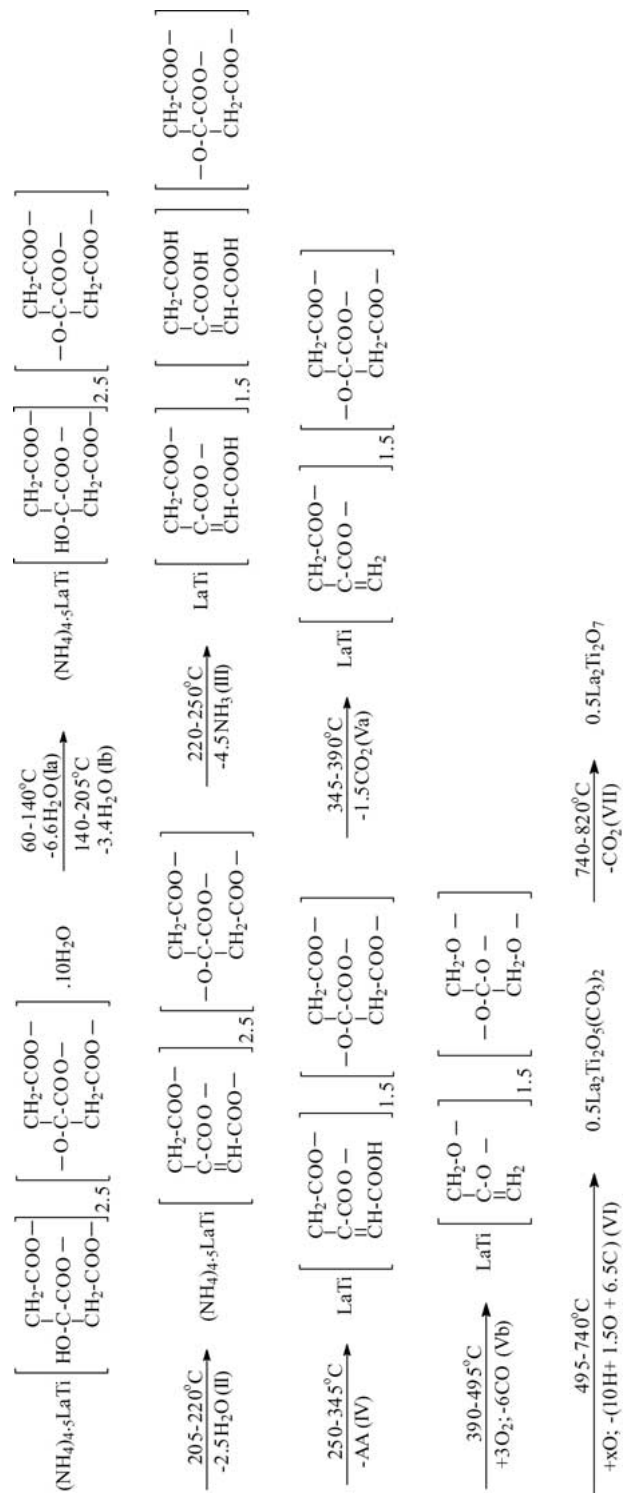
[d] See Figs 1–6.

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LaTi $\left[\begin{array}{c} CH_2-COOROH \\ HO-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-COOROH \\ CH_2-COO-R-OOC-CH_2 \end{array}\right.$ $\begin{array}{c} CH_2-COO- \\ -O-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-COO \\ R-OOC-CH_2 \end{array}$ $\begin{array}{c} CH_2-COO- \\ HO-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-COO- \\ R-OOC-CH_2 \end{array}$ $\begin{array}{c} CH_2-COOROH \\ -O-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-COOROH \\ CH_2-COO-R-OOC-CH_2 \end{array}$ $\left.\begin{array}{c} CH_2-COO- \\ -O-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-COOROH \\ CH_2-COOROH \end{array}\right]_{0.5}$ .0.4HOROH .5H_2O

$\xrightarrow[\substack{50-142^oC \\ -4H_2O \text{ (Ia)} \\ 140-170^oC \\ -H_2O \text{ (Ib)}}]{}$ LaTi $\left[\begin{array}{c} CH_2-COOROH \\ HO-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-COOROH \\ CH_2-COO-R-OOC-CH_2 \end{array}\right.$ $\begin{array}{c} CH_2-COO- \\ -O-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-COO \\ HO-OOC-CH_2 \end{array}$ $\begin{array}{c} CH_2-COO- \\ HO-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-COOROH \\ R-OOC-CH_2 \end{array}$ $\left.\begin{array}{c} CH_2-COO- \\ -O-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-COOROH \\ CH_2-COOROH \end{array}\right]_{0.5}$ .0.4HOROH

$\xrightarrow[\substack{170-200^oC \\ -1.5H_2O \text{ (II)}}]{}$ LaTi $\left[\begin{array}{c} CH_2-COOROH \\ \overset{\displaystyle |}{\underset{\displaystyle |}{C}}-COOROH \\ CH-COO-R-OOC-CH \end{array}\right.$ $\begin{array}{c} CH_2-COO- \\ -O-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-COO \\ R-OOC-CH_2 \end{array}$ $\begin{array}{c} CH_2-COOROH \\ -O-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-COOROH \\ R-OOC-CH_2 \end{array}$ $\left.\begin{array}{c} CH_2-COO- \\ -O-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-COOROH \\ CH_2-COOROH \end{array}\right]_{0.5}$ .0.4HOROH

$\xrightarrow[\substack{200-235^oC \\ -0.4HOROH \text{ (IIIa)} \\ 235-280^oC \\ -3.5RO \text{ (IIIb)}}]{}$ LaTi $\left[\begin{array}{c} CH_2-COOH \\ \overset{\displaystyle |}{\underset{\displaystyle |}{C}}-COOH \\ CH-COO-R-OOC-CH \end{array}\right.$ $\begin{array}{c} CH_2-COO- \\ -O-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-COO \\ R-OOC-CH_2 \end{array}$ $\begin{array}{c} CH_2-COO- \\ -O-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-COOH \\ R-OOC-CH_2 \end{array}$ $\left.\begin{array}{c} CH_2-COO- \\ -O-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-COO- \\ CH_2-COOH \end{array}\right]_{0.5}$

$\xrightarrow[\substack{280-370^oC \\ -[2(CH_2)\text{ (IIIc)}+7.5CO_2+C_3H_6\text{[IV]}]}]{}$ LaTi $\left[\begin{array}{c} CH_2-COOH \\ \overset{\displaystyle |}{\underset{\displaystyle |}{C}}-COOH \\ -O-CH \\ CH_3 \end{array}\right.$ $\left.\begin{array}{c} CH_2-COO- \\ \overset{\displaystyle |}{\underset{\displaystyle |}{C}}-COO- \\ CH_2 \end{array}\right]_{1.5}$ $\left.\begin{array}{c} CH_2-COO- \\ -O-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-COO- \\ CH_3 \end{array}\right]_{0.5}$

$\xrightarrow[\substack{370-485^oC \\ +xO_2; -4.5CO\text{(Va)}}]{}$ LaTi $\left[\begin{array}{c} CH_2-O- \\ -O-CH \\ CH_3 \end{array}\right.$ $\left.\begin{array}{c} CH_2-O- \\ C-O- \\ \overset{\displaystyle ||}{CH_2} \end{array}\right]_{1.5}$ $\left.\begin{array}{c} CH_2-O- \\ -O-C-O- \\ CH_3 \end{array}\right]_{0.5}$

$\xrightarrow[\substack{485-435^oC \\ +6.5O_2 \\ -(16H+1.5O)\text{ (V)}}]{}$ 8C + 0.5La_2Ti_2O_5(CO_3)_2 $\xrightarrow[\substack{425-750^oC \\ +xO_2; \\ -(9C+2O)\text{ (VI, VII)}}]{}$ 0.5La_2Ti_2O_7

Figure 5 Supposed scheme of the thermal decomposition of the La-Ti-citrate prepared in EG-medium (LaTiC120).

$(NH_4)_{4.5}LaTi \left[\begin{array}{c} CH_2-COO- \\ HO-C-COO- \\ CH_2-COO- \end{array} \right]_{2.5} .10H_2O$

$\xrightarrow[-2.5H_2O (II)]{205-220^oC}$

$(NH_4)_{4.5}LaTi \left[\begin{array}{c} CH_2-COO- \\ C-COO- \\ \parallel \\ CH-COO- \end{array} \right]_{2.5}$

$\xrightarrow[-AA (IV)]{250-345^oC}$

$LaTi \left[\begin{array}{c} CH_2-COO- \\ C-COO- \\ \parallel \\ CH-COOH \end{array} \right]_{1.5}$

$\xrightarrow[+3O_2; -6CO (Vb)]{390-495^oC}$

$LaTi \left[\begin{array}{c} CH_2-O- \\ C-O- \\ \parallel \\ CH_2 \end{array} \right]_{1.5}$

$\xrightarrow[+xO; -(10H+1.5O+6.5C)(VI)]{495-740^oC}$

$0.5La_2Ti_2O_5(CO_3)_2$

$\xrightarrow[60-140^oC\ -6.6H_2O (Ia)\ \ 140-205^oC\ -3.4H_2O (Ib)]{}$

$(NH_4)_{4.5}LaTi \left[\begin{array}{c} CH_2-COO- \\ HO-C-COO- \\ CH_2-COO- \end{array} \right]_{2.5}$

$\left[\begin{array}{c} CH_2-COO- \\ -O-C-COO- \\ CH_2-COO- \end{array} \right]$

$\xrightarrow[-4.5NH_3 (III)]{220-250^oC}$

$(NH_4)_{4.5}LaTi \left[\begin{array}{c} CH_2-COO- \\ -O-C-COO- \\ CH_2-COO- \end{array} \right]_{2.5}$

$LaTi \left[\begin{array}{c} CH_2-COOH \\ C-COOH \\ \parallel \\ CH-COOH \end{array} \right]_{1.5}$

$\xrightarrow[-1.5CO_2 (Va)]{345-390^oC}$

$LaTi \left[\begin{array}{c} CH_2-COO- \\ C-COO- \\ \parallel \\ CH_2 \end{array} \right]_{1.5}$

$\left[\begin{array}{c} CH_2-COO- \\ -O-C-COO- \\ CH_2-COO- \end{array} \right]_{1.5}$

$\xrightarrow[-CO_2 (VII)]{740-820^oC}$

$0.5La_2Ti_2O_7$

$\left[\begin{array}{c} CH_2-COO- \\ -O-C-COO- \\ CH_2-COO- \end{array} \right]$

Figure 6 Supposed scheme of the thermal decomposition of the NH_4-La-Ti prepared in H_2O medium (LaTiC40w); AA-aconitic acid.

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TABLE IV Content of H and C (%) in some of the intermediates from the heating of La- Ti-citrate, prepared in EG

Temperature of heating (°C)	H		C	
	Fᵃ	Cᵃ	F	C
Initial sample	4.54	4.40	34.04	33.87
240	3.90	3.58	37.64	37.28
350	3.22	2.75	29.48	27.63

ᵃF-experimentally found; C-calculated according to the scheme on Fig. 5.
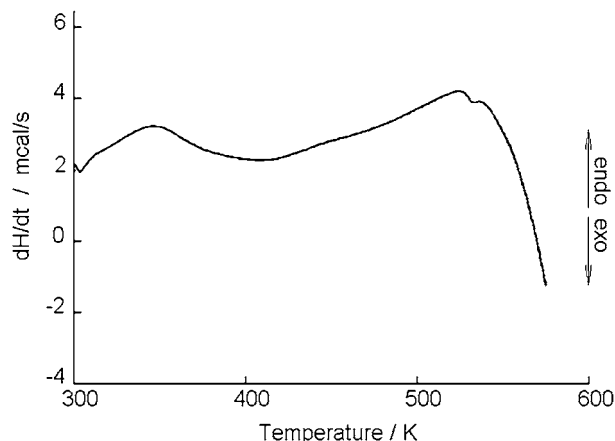
Figure 7 DSC-study of the La-Ti-citrate prepared in EG (LaTiC120); see the text for the symbol used.

heated at 240°C (see Fig 8). The H and C contents in the intermediate obtained at 240°C (see Table IV) agree with the proposed process scheme (see Fig. 5). As the ^{1}H-NMR spectrum (see Fig. 9) shows, the esters are preserved but are already disturbed at this temperature.

The DTA curve on Fig. 3 suggests that *the deesterification* (stages III b, c, Fig. 5) proceeds in two steps probably first with the destruction of COOROH fragments and then of COOROOC (see Figs 1 and 3; Table III). This supposition is in accord with the higher temperature of the ester destruction for the Sr-Ti-polyester resin [2]. For some samples it is difficult to distinguish these steps from the separation of the EG or/and the following decarboxilation. The deesterification leads to a replacement of the absorption maximum at 1736 cm^{-1} that belongs to the C=O stretching vibration of ester groups [25] (see Fig. 8) by the COOH band at ∼1700 cm^{-1}. As can be expected, the DSC curve (see Fig. 7) shows that, stages IIIa and b are endothermic. The exoeffect above 250°C is due to the EG and/or its decomposition products interaction with the oxygen from air (The pure EG burns at 210–280°C).

The DTG and DTA curve patterns in the 200–280°C region are, naturally, rather different from those for the La-Ti-citrates, obtained in EG and in water (see Figs 3 and 4).

The *decarboxilation* of COOH groups (stage IV on Fig. 5, and Va on Fig. 6), that results from the deesterification takes place at 250–370°C (see Table III). The H- and C-contents in the residue from LaTiC120 (see Table IV) confirm the supposed processes (see Fig. 5). The band at 1700 cm^{-1} in the same sample spectrum (see Fig. 8) exhibits only as a shoulder. From the po-
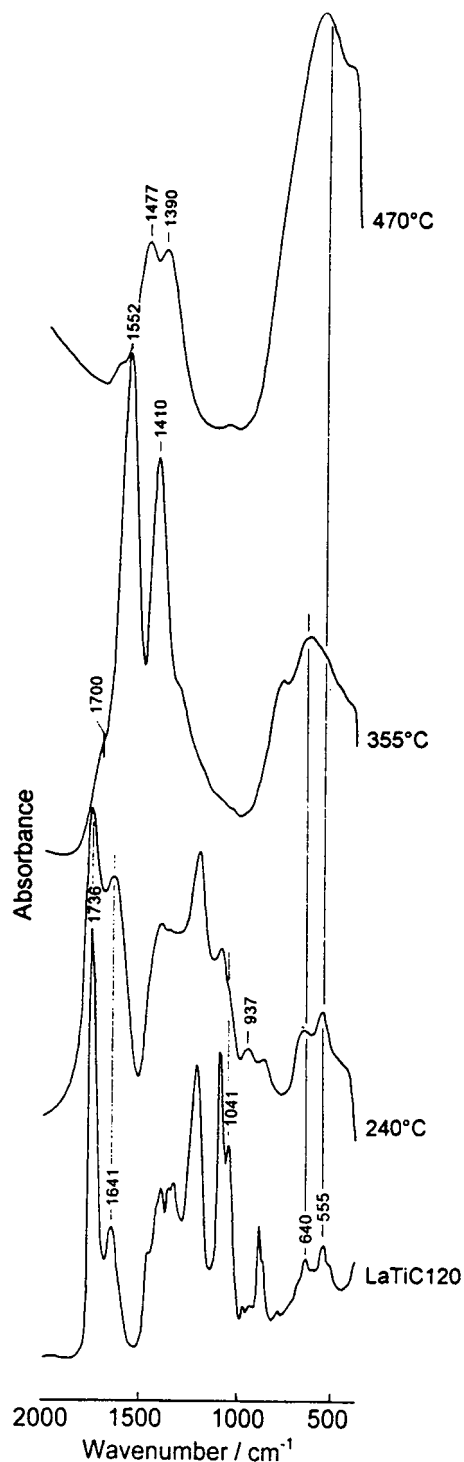
Figure 8 IR-spectra of the La-Ti-citrate prepared in EG (LaTiC120) (1) and of the intermediates obtained at heating (10°C/min) to 240°C (2), 350°C (3), 470°C (4).

sition of the COO$^-$ bands (ν^{as} at 1552 cm^{-1} and ν^s at 1410 cm^{-1}) it follows that carboxylate groups in the intermediate act as bidentate ligand groups.

Our results concerning stages III and IV are in accordance with the more general data concerning mass loss during the heating of the polyester resins as a result of the PCM application for some systems [2, 6, 8–10]. The formation of itaconate (see Figs 5 and 6) is found also for the Ba-Ti-citrate decomposition products [16]. However we did not find evidence (at least in the case of La- and La-Ti-citrate derivatives) of the formation of itaconic anhydride that was found by the same authors.
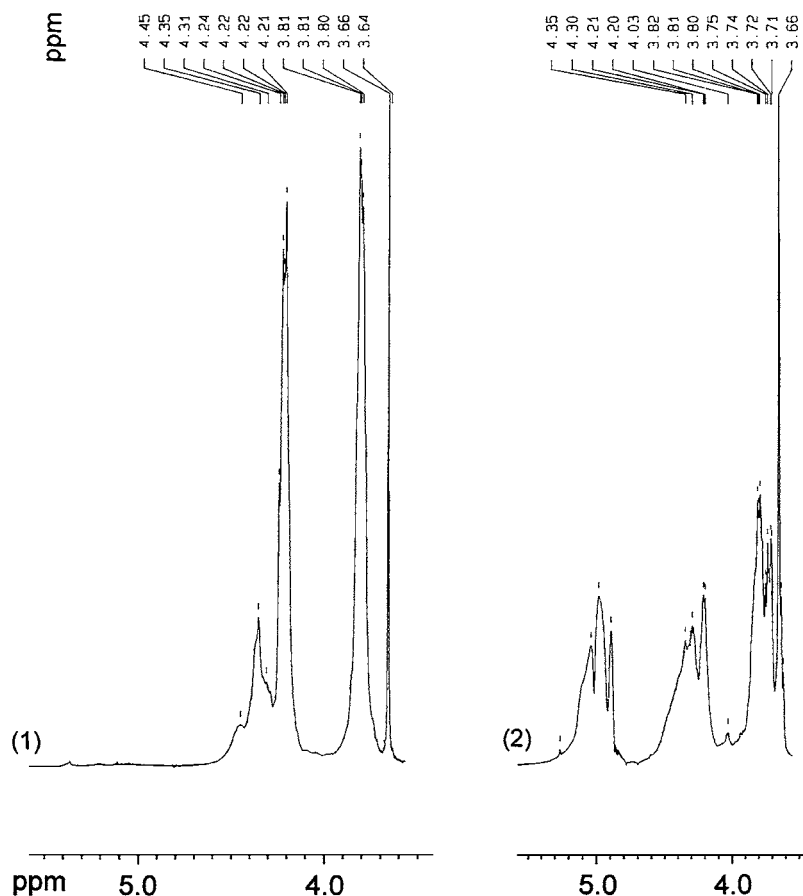
Figure 9 ^{1}H- NMR spectra (fragments) of the initial La-Ti citrate (LaTiC120) (1) and of the same complex heated (10°C/min) to 240°C (2).

During step (V on Fig. 5), up to 420–535°C, *the complete destruction of the organic skeleton* takes place. The bands belonging to CO_3^{2-} and/or oxocarbonates and to Ti-O are the only ones observed in the IR-spectrum of the product that was obtained as a result of the La-Ti-citric complex decomposition at 470°C (see Fig. 8). The shoulder at 1608 cm^{-1} had also been found in an earlier study [2], and had been related to an unidentified product of the polyester resin destruction. However, along with the weak broad band at ~3400 cm^{-1},

the shoulder may be due to H_2O adsorbed during the storage of the sample before the analysis. H_2O may form hydrates of the carbonates, and it could explain the little higher mass loss in the following stage (see Table III). The gray color of the residue confirms the presence of residual carbon. The process proceeds stepwise excluding Ti- complex (see Figs 5 and 6).

The nature of the compounds formed at the end of this, or analogous stages, has been discussed in the literature. According to an earlier study [16], $BaCO_3$ and
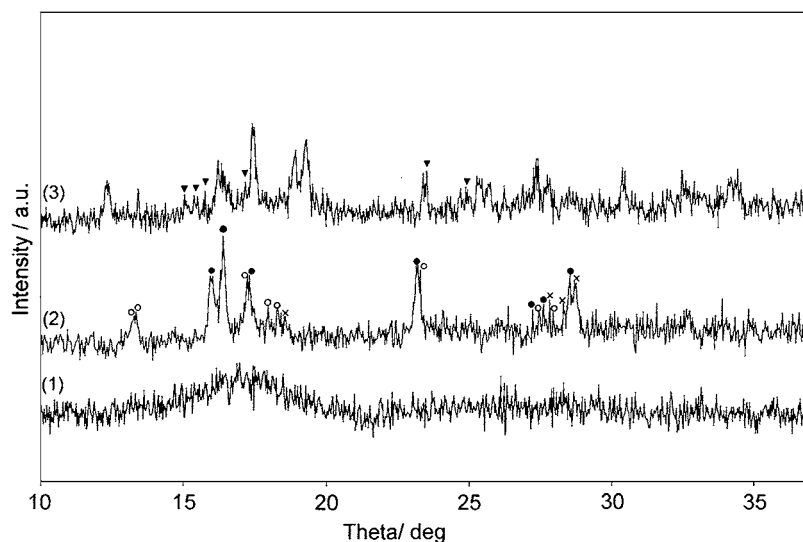
Figure 10 X-ray powder diffractograms of the La-Ti-citrate, prepared in EG (LaTiC120), heated at 550°C(1) and 670°C (3), and of La-citrate (LaC120), heated at 550°C (2); ○- $La_2O_2CO_3$, ●- $La_2O(CO_3)_2$, ▼, ✕ - unidentified phases.

TiO_2 are formed from a Ba-Ti-citrate. The formation of $Ba_2Ti_2O_5CO_3$ was accepted in [3], and confirmed by IR and X-ray data [5, 6].

The formation of an analogous $La_2Ti_2O_5(CO_3)_2$ is assumed in the process schemes (see Figs 5 and 6). From the point of view of ionic radia values, the formation of such a compound is even more probable than the formation of $Ba_2Ti_2O_5CO_3$. Along with the mass loss at stages V–VII, few other facts support the assumption regarding the formation of a mixed-metal carbonate: (i) The presence of CO_3^{2-} is undoubtedly proved by the IR data (see Fig. 8). (ii) The same spectra do not confirm the formation of TiO_2- the position of the Ti-O band maximum (580 cm^{-1}) is apparently different from that of anatase (640 cm^{-1} [3]). (iii) XRD and IR spectral data suggest that the intermediates obtained from uni- and bimetallic compounds are rather different. (iv) In contrast with the La-Ti-decomposition product, obtained from the bimetallic complex after heating for 90 min at 550°C, which remains X-ray amorphous, the La- product in the same conditions crystallizes into a mixture of $La_2O(CO_3)_2$, $La_2O_2CO_3$, an unidentified (probably metastable) phase accompanied by amorphous LaOHCO$_3$ (see Fig. 10). Carbonization of the $La_2O_2CO_3$ during the storage of the heated sample may contribute to the content of $La_2O(CO_3)_2$ in the intermediate. The LaOHCO$_3$, resulting from easy hydration of the highly energetic surface of "fresh-prepared" $La_2O_2CO_3$ [26], is detected on the basis of the IR absorption maximum of δ(La-OH) at 627 cm^{-1} (see Fig. 11), along with a sharp, intense band at 3600 cm^{-1} due to the stretching mode of hydroxide ions [27]. Such bands are absent in the bimetallic compound spectrum (see Fig. 11). As a whole, the IR spectra of the above-mentioned samples (see Fig. 11) can not be explained by the difference in their degree of crystallization only.

The burning of the residual carbon (VI) turns samples white. It seems that the process, especially for the monometallic complexes, consists of several steps (see Fig. 1).

The decomposition of the oxocarbonates (stage VII) is clearly developed for the La-citrate (see Fig. 1). For the bimetallic system (see Fig. 3), it can be related to the broad DTG-peak around 750°C. The process is more transparent for the mixed-metal systems with lower C-content, prepared in water (see Fig. 4), or in EG-medium but with a lower degree of esterification due to the lower (40°C) temperature of heating for the initial solution [28]. The mass loss in this temperature interval has also been found for the polyester resin-precursors of $La_2Ti_2O_7$ (>780°C), $Nd_2Ti_2O_7$ (829°C) [7], and BaTiO$_3$ [3].

It should be noted that the mass decrease during the heating of Ti-citrate (see Fig. 3) is practically completed at 650°C, but for the La-citrate (see Fig. 2) this temperature is 820°C due to the formation of the thermally stable oxocarbonate. Poorly crystallized $La_2Ti_2O_7$ is produced at 670°C, and unidentified peaks, most probably of supposed $La_2Ti_2O_5(CO_3)_2$, are observed in the X-ray diffractogram (see Fig. 10). Carbonates are still present in trace amounts up to 750°C, but they are bet-

ter detected by IR- spectroscopy (see Fig. 11). The IR spectrum of La-Ti-citrate that was heated at 850°C (see Fig. 11) contains only absorption maximums for $La_2Ti_2O_7$ [29].

The elemental analysis and X-ray powder diffractometry [19] also proved the phase-homogeneity of the final $La_2Ti_2O_7$.

The release of NH$_3$ from water-prepared NH$_4$-La-Ti -citrate (see Fig.4) takes place just after the intramolecular dehydration (stage III on Fig. 6 and Table III). The newly-formed aconitic acid causes the appearance of a band at 1700 cm^{-1} in the sample IR spectrum. The analogous effect has been observed for NH$_4$-Li-Co-citrate derivatives [17]. The mass-loss accompanied by an exothermic effect in the interval 250–350°C suggests that the free aconitic acid decomposes completely in this interval (stage IV in Fig. 6 and Table III). The
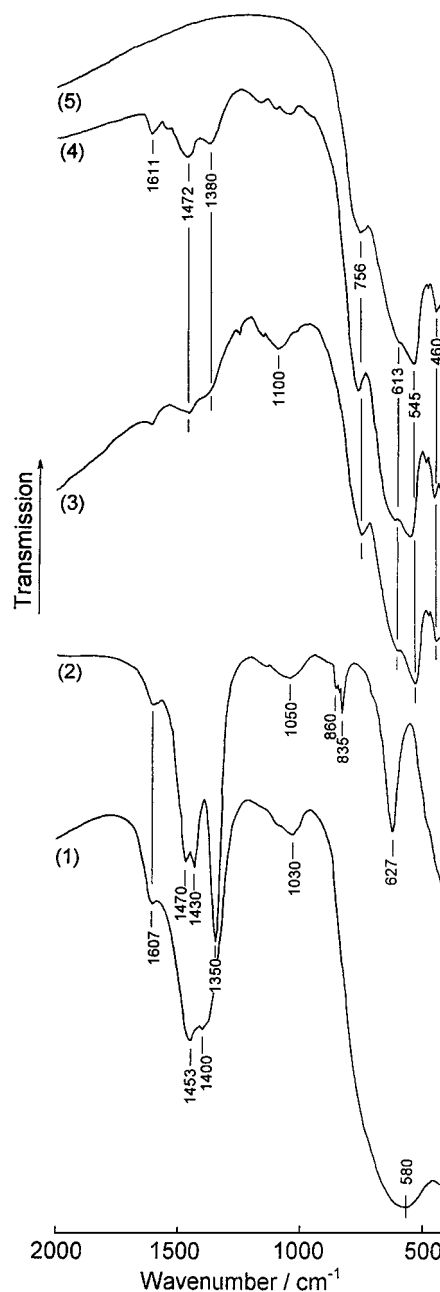

Figure 11 IR-spectra of the La-Ti-citrate, prepared in EG (LaTiC120), heated at 550°C(1), 670°C (3), 750°C (4) and at 850°C for 4 h (5) and La-citrate (LaC120), heated at 550°C (2).

following stages are analogous to the ones proposed in Fig. 5.

4. Conclusion
The reported study reveals the main stages of the thermal decomposition of La-, Ti- and La-Ti-citrates, obtained in EG-medium, as well as of NH_4-La-Ti-citrate prepared in water solution. The comparison of the behavior of the individual complexes and of the bimetallic one, especially in the final stages of the process provides evidence against the hypothesis concerning formation of the final titanate by a solid state reaction between individual La- and Ti-compounds.

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