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$M^{II}TiO(C_2O_4)_2 \cdot 4H_2O$ (M^{II} = Mg, Ca, Sr OR Ba) AS PRECURSORS IN THE FORMATION OF $M^{II}TiO_3$ POWDERS

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A synthesis route is described for the preparation of the alkaline earth metal titanyl oxalates $M^{II}TiO(C_2O_4)_2 \cdot 4H_2O$ (M^{II} = Mg, Ca, Sr or Ba). The thermal decompositions of these compounds were studied by means of DTA and TG in comparison with X-ray measurements. The final products $M^{II}TiO_3$ were characterized morphologically.

$BaTiO_3$, $SrTiO_3$, $CaTiO_3$ and $MgTiO_3$ powders are very interesting substances for electroceramic applications. Their properties are strongly influenced by the conditions of preparation. The wet chemical route for the synthesis of the titanates has some advantages for the final products, e.g. for the morphologic and analytical properties, and hence for the sintering behaviour.

One method for the synthesis of alkaline earth metal titanates $M^{II}TiO_3$ (M^{II} = Mg, Ca, Sr or Ba) by the wet chemical route is precipitation of the corresponding titanyl oxalates and their subsequent decomposition. The preparation and thermal decomposition of $BaTiO(C_2O_4)_2 \cdot 4H_2O$ are already well known [1]. Several authors have investigated the formation of $BaTiO_3$ from titanyl oxalate by using DTA, TG or ETA [2–8]. Information is also available on the thermal decomposition of $SrTiO(C_2O_4)_2 \cdot 4H_2O$ [3, 4]. On the other hand, there is only little or no knowledge on the analogous compounds of Ca and Mg.

The aim of this work was to study the preparation of the titanyl oxalates of Mg, Ca, Sr and Ba by a new route and to investigate the decomposition reactions by means of thermoanalytical methods (TG and DTA) in combination with X-ray measurements. The titanate powders were characterized through the use of electron microscopy and granulometry.

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Experimental

Preparation of the compounds

Aqueous ammonia was added to an ethanolic solution of oxalic acid until a pH of 3.0 was reached. A solution of "$M^{II}TiCl_6$", prepared by dissolving $M^{II}Cl_2$ and $TiCl_4$ in water, was added dropwise at a constant pH of 3.0 at 55° to the oxalic acid solution. The mole ratio applied was M^{II} : Ti : $(COOH)_2$ = 1.00 : 1.00 : 2.40.

The white precipitates obtained were filtered off and washed until all chloride had disappeared. The substances were dried in a desiccator over concentrated H_2SO_4. The analytical composition of all four compounds was $M^{II}TiO(C_2O_4)_2 \cdot 4H_2O$.

Methods

The thermal decompositions of the four alkaline earth metal titanyl oxalates were studied by using DTA (Rigaku Thermoflex), TG (electromagnetic compensated thermobalance) [9] and X-ray diffraction.

Results

Thermal decompositions of the compounds $M^{II}TiO(C_2O_4)_2 \cdot 4H_2O$

Figures 1–4 show the TG, DTG and DTA curves of $MgTiO(C_2O_4)_2 \cdot 4H_2O$, $CaTiO(C_2O_4)_2 \cdot 4H_2O$, $SrTiO(C_2O_4)_2 \cdot 4H_2O$ and $BaTiO(C_2O_4)_2 \cdot 4H_2O$, together with the diffractograms of the decomposition products at certain temperatures. The measurements were completed at 900°. Whereas the results for the Ca, Sr and Ba compounds are very similar, $MgTiO(C_2O_4)_2 \cdot 4H_2O$ exhibits a different behaviour.

The decomposition takes place in several steps, as is already known for the titanyl oxalates of Ba and Sr [2–8]. Table 1 gives an outline of the separate steps and an interpretation of the chemism with the help of equations for the Ca, Sr and Ba compounds on the one hand, and the Mg species on the other.

The X-ray diffractograms show that the substances $M^{II}TiO(C_2O_4)_2 \cdot 4H_2O$ (M^{II} = Ca, Sr or Ba) are amorphous compounds, but $mgTiO(C_2O_4)_2 \cdot 4H_2O$ is crystalline. At 500° all four decomposition products display reflexes in their diffractograms (Figs 1–4). For the Ca, Sr and Ba compounds, the carbonates $M^{II}CO_3$ and TiO_2 (rutile) are present at this temperature, whereas the reflexes of MgO and $MgTi_2O_5$ can be observed in the case of the Mg species. $MgCO_3$ is already decomposed at 500°. At higher temperatures, the compounds $M^{II}TiO_3$ are formed. The $M^{II}TiO_3$ species (M^{II} = Ca, Sr or Ba) are produced quantitatively

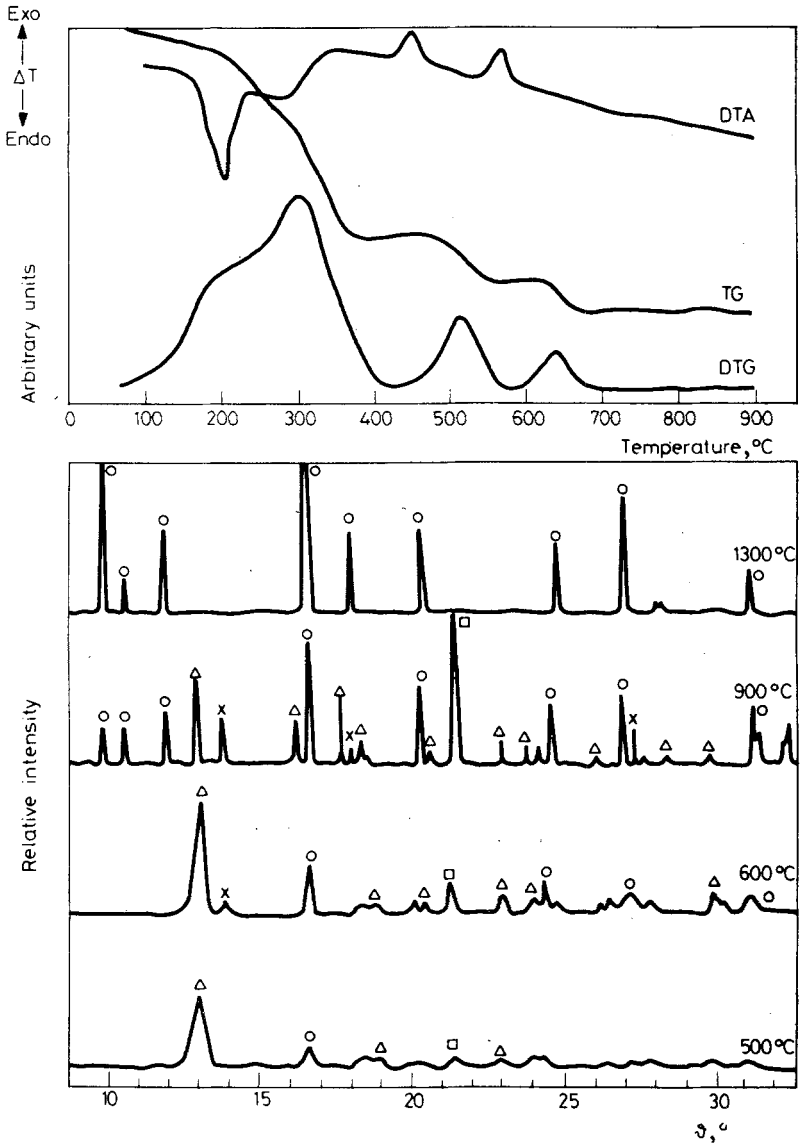

Fig. 1 DTA, TG and DTG curves of $MgTiO(C_2O_4)_2 \cdot 4H_2O$ together with the diffractograms of the decomposition products at 500 °C, 600 °C, 900 °C, and 1300 °C (in each case 15 h decomposed). ○ $MgTiO_3$, □ $MgTi_2O_5$, × TiO_2 (rutile), △ MgO

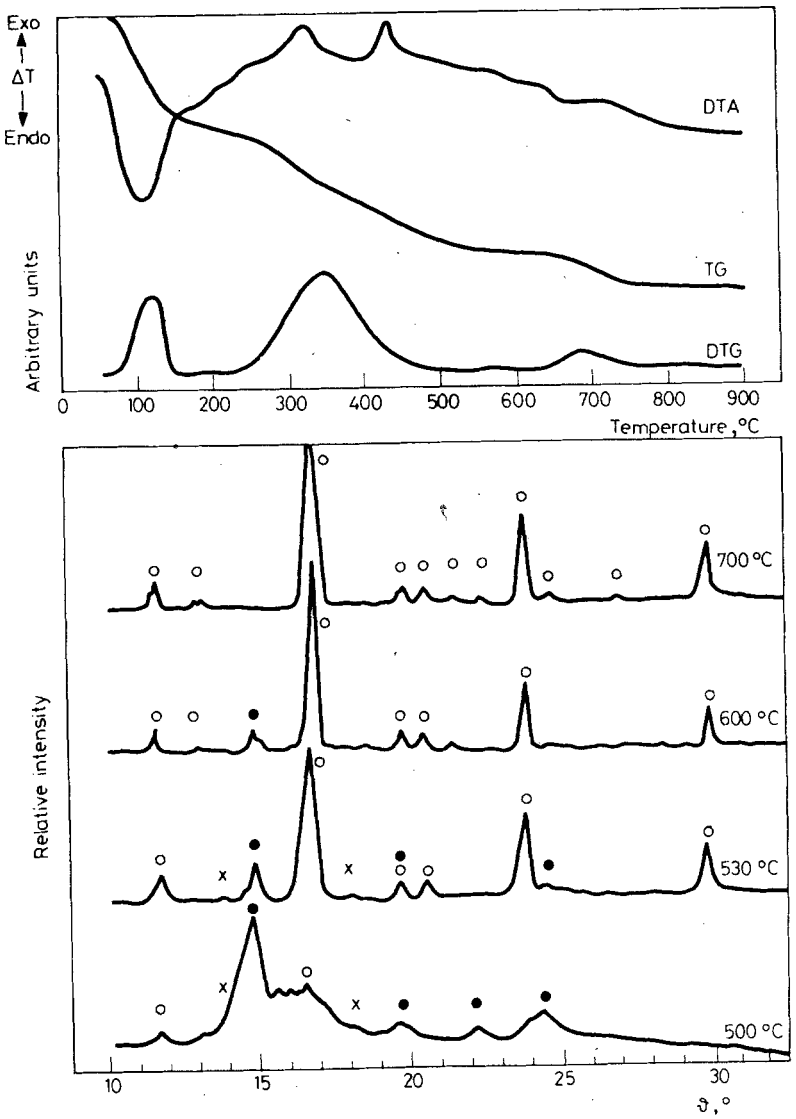

Fig. 2 DTA, TG and DTG curves of $CaTiO(C_2O_4)_2 \cdot 4\,H_2O$ together with the diffractograms of the decomposition products at 500 °C, 530 °C, 600 °C, and 700 °C (in each case 15 h decomposed). ○ $CaTiO_3$, ● $CaCO_3$, × TiO_2 (rutile)

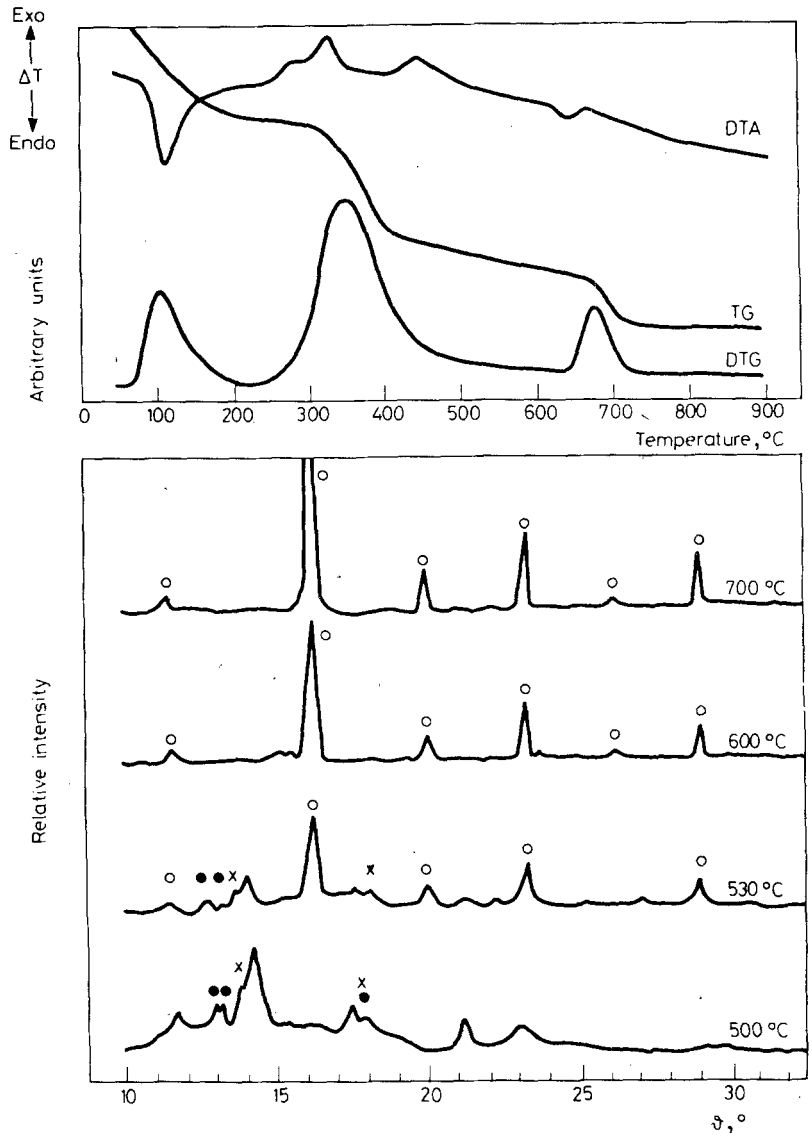

Fig. 3 Analogous Fig. 2 for $SrTiO(C_2O_4)_2 \cdot 4H_2O$. ○ $SrTiO_3$, ● $SrCO_3$, × TiO_2 (rutile)

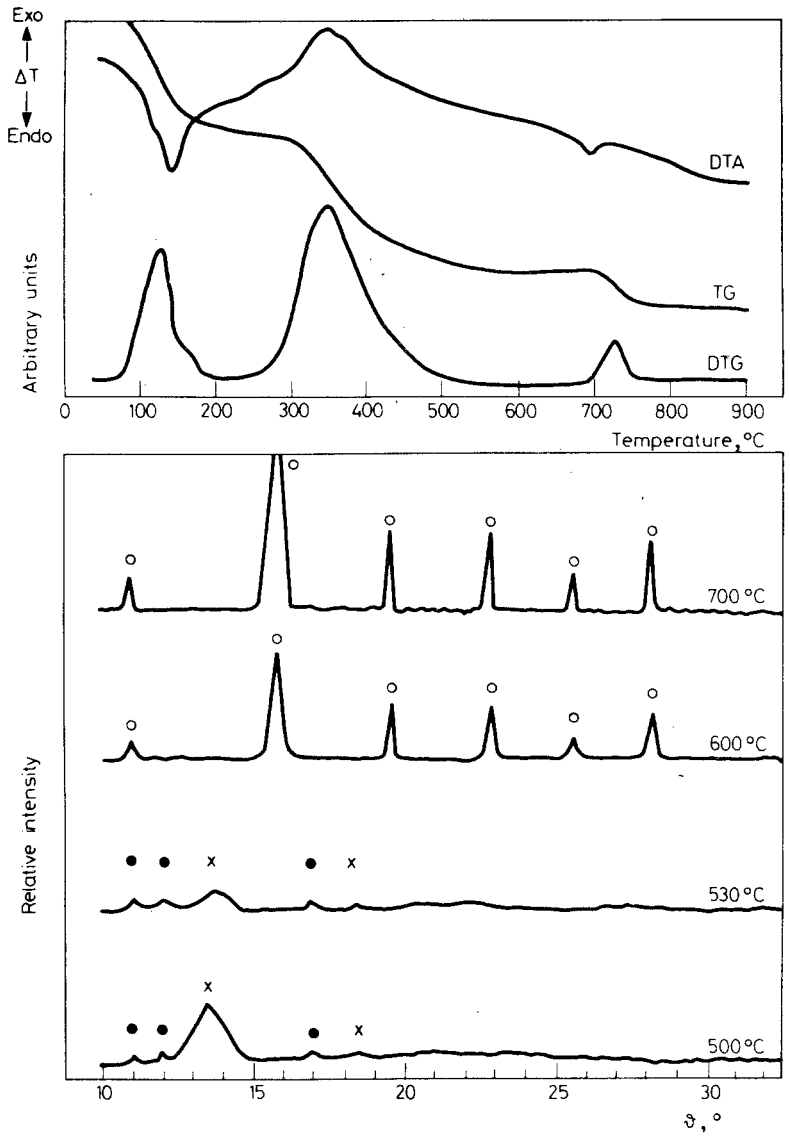

Fig. 4 Analogous Fig. 2 for $BaTiO(C_2O_4)_2 \cdot 4H_2O$. ○ $BaTiO_3$, ● $BaCO_3$, × TiO_2 (rutile)

after 15 h at 700°. To get pure $MgTiO_3$, it is necessary to increase the temperature to 1300°. TiO_2 (rutile) is also an intermediate (at temperatures higher than 600°).

Figure 5 (a)–(d) shows electron micrographs of $MgTiO_3$ decomposed for 1 h at 1300° and of $CaTiO_3$, $SrTiO_3$ and $BaTiO_3$ all decomposed for 1 h at 900°. Whereas

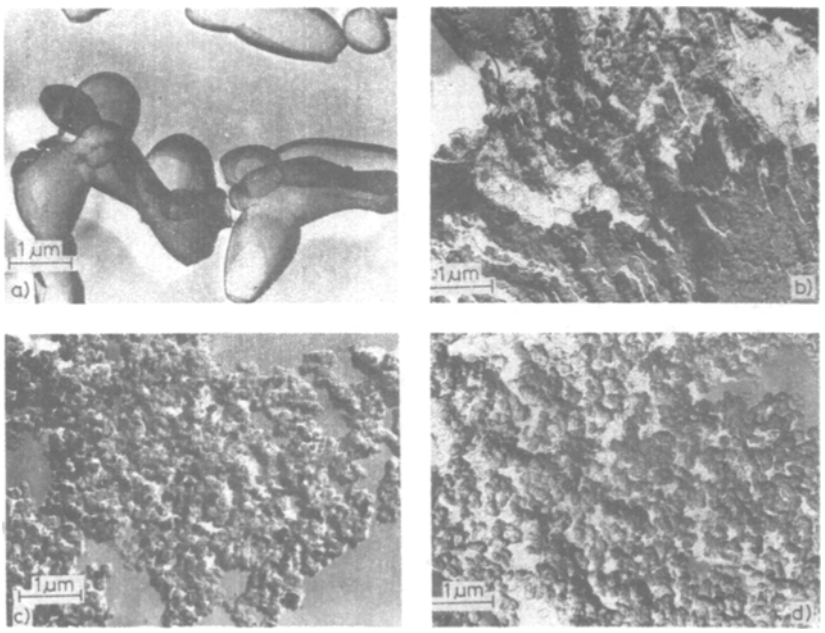

Fig. 5 Electron micrographs of (a)–(d). (a) $MgTiO_3$ (1 h 1300 °C), (b) $CaTiO_3$ (1 h 900 °C), (c) $SrTiO_3$ (1 h 900 °C), (d) $BaTiO_3$ (1 h 900 °C)

the Mg compound has large grains, the others consist of very small particles, and they are strongly agglomerated. The morphological parameters are listed in Table 2.

Conclusions

It is possible to prepare the substances $M^{II}TiO(C_2O_4)_2 \cdot 4H_2O$ (M^{II} = Mg, Ca or Sr) in the same way as $BaTiO(C_2O_4)_2 \cdot 4H_2O$. The thermal decomposition behaviour is similar for the Ca, Sr and Ba compounds, but different for the Mg species. The carbonates of Ca, Sr and Ba together with TiO_2 (rutile) are the intermediates in the former group, whereas MgO, $MgTi_2O_5$ and TiO_2 (rutile) can be observed for the Mg complex. The formation of $CaTiO_3$, $SrTiO_3$ and $BaTiO_3$ is complete at 700° but that of $MgTiO_3$ requires a temperature of 1300°.

Table 1 Summary of the results obtained by thermal analysis

$M^{II}TiO(C_2O_4)_2 \cdot 4\,H_2O$ (M^{II}: Ca, Sr, Ba)	$MgTiO(C_2O_4)_2 \cdot 4\,H_2O$
DTA: endothermic effect from 100 °C to 180 °C	DTA: endothermic effect from 100 °C to 180 °C
TG: mass loss until 200 °C	TG: mass loss until 200 °C
$M^{II}TiO(C_2O_4)_2 \cdot 4\,H_2O \rightarrow M^{II}TiO(C_2O_4)_2 + 4\,H_2O$	$MgTiO(C_2O_4)_2 \cdot 4\,H_2O \rightarrow MgTiO(C_2O_4)_2 + 4\,H_2O$
DTA: exothermic effect(s) from 300 °C to 600 °C	DTA: exothermic effects from 200 °C to 700 °C
TG: mass loss until 550 °C	TG: mass loss until 700 °C
$M^{II}TiO(C_2O_4)_2 + \frac{1}{2}O_2 \rightarrow M^{II}CO_3 + TiO_2 + 2\,CO_2 + CO$	$MgTiO(C_2O_4)_2 + \frac{1}{2}O_2 \rightarrow$ "$MgO + TiO_2$" $+ 3\,CO_2 + CO$
DTA: endothermic effect at 650 °C (Ca, Sr) and 700 °C (Ba)	DTA: no measurable effects from 700 °C to 900°C
TG: mass loss until 750 °C	TG: no mass loss above 700 °C
$M^{II}CO_3 + TiO_2 \rightarrow M^{II}TiO_3 + CO_2$	"$MgO + TiO_2$" $\xrightarrow{1300\ °C}$ $MgTiO_3$

Table 2 Parameters of the morphology of $MgTiO_3$, $CaTiO_3$, $SrTiO_3$ and $BaTiO_3$. Specific surface S_{BET} and average particle diameter d_{BET} obtained by BET technique, and particle diameter range d_{elmi} found by electronmicroscopy

Compound (conditions of decomposition)	S_{BET}, m^2/g	d_{BET}, μm	d_{ELMI}, μm
$MgTiO_3$ (1 h 1300 °C)	1	1.53	0.4 – 2.7
$CaTiO_3$ (1 h 900 °C)	12	0.12	0.05–0.15
$SrTiO_3$ (1 h 900 °C)	21	0.06	0.02–0.15
$BaTiO_3$ (1 h 900 °C)	9	0.11	0.05–0.2

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Zusammenfassung — Ein Syntheseweg für die Darstellung der Erdalkalimetalltitanyloxalate $M^{II}TiO(C_2O_4)_2 \cdot 4H_2O$ (M^{II} = Mg, Ca, Sr, Ba) wird beschrieben. Die thermische Zersetzung dieser Verbindungen wurde mittels DTA und TG sowie Röntgenbeugungsmethoden untersucht. Die entstehenden Titanate $M^{II}TiO_3$ wurden hinsichtlich ihrer morphologischen Eigenschaften charakterisiert.

Резюме — Описан путь синтеза двойных оксалатных солей титанила и щелочно-земельных металлов общей формулы $M^{II}TiO(C_2O_4)_2 \cdot 4H_2O$, где M^{II} = магний, кальций, стронций и барий. Термическое разложение солей было изучено методами ДТА, ТГ и рентгенофазовым анализом. Морфологически охарактеризованы $M^{II}TiO_3$, как конечные продукты разложения.