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THERMAL DECOMPOSITION OF CALCIUM AND STRONTIUM PEROXOTITANATES TO METATITANATES

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Abstract

Methods of DTA, TG, DSC, IR spectroscopy and X-ray phase analysis were used to study the thermal dehydration and decomposition of Ca^{2+} and Sr^{2+} peroxotitanates to the corresponding metatitanates. The stages of the process and the intermediate phases were identified. The information obtained was utilised to determine the optimum temperatures of heating of the initial peroxotitanates to yield metatitanates with a fairly high degree of crystallinity (for $CaTiO_3$ 680°C, and for $SrTiO_3$ 650°C).

Keywords: metatitanates, peroxotitanates, thermal decomposition

Introduction

The investigations presented are a contribution to research relating to the synthesis and properties of the peroxotitanates of certain bivalent metals, used to obtain the corresponding metatitanates.

An earlier publication [1] described the conditions of synthesis of calcium and strontium peroxotitanates, $Ca_2[Ti_2(O_2)_4(OH)_4]\cdot 4H_2O$ and $Sr_2[Ti_2(O_2)_4(OH)_4]\cdot 3H_2O$. The pertinent literature contains data on similar compounds, but with different compositions, obtained under conditions different from those described in this article. For instance, the authors of [2] describe compounds with composition $M_2[Ti_2(O_2)_4(OH)_2]\cdot H_2O$, $M^{2+}=Ca^{2+}$, Sr^{2+} and Ba^{2+}, while the authors of [3] report on $SrTiO(OH)_4$. Their TG, DTG and DTA curves have been taken, while in [2] the corresponding IR spectra of the examined compounds were recorded as well.

Experimental

Calcium and strontium peroxotitanates were obtained as amorphous precipitates by a method described earlier [1]. They were identified by methods of

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quantitative analysis: titanium was determined gravimetrically [4], calcium and strontium complexometrically [5], peroxide groups permanganometrically [6], hydroxy groups by Chernev's method [7], and water by Fisher's method [8].

The TG, DTG and DTA curves of the initial and intermediate samples were recorded on Perkin-Elmer equipment at a heating rate of 10 deg·min^{-1} up to 900°C, while the corresponding DSC curves were obtained on equipment of the same firm at a heating rate of 20 deg·min^{-1} in the temperature interval 50–450°C. The IR spectra were taken with a Zeiss IR-70 spectrophotometer, in the interval 4000–400 cm^{-1}, in KBr tablets, while in the regions of the water stretching vibrations they were taken as suspensions in hexachloro-1,3-butadiene. The X-ray phase data were obtained with a Zeiss TUR-M-62 goniometer, with CuK$_\alpha$ radiation.

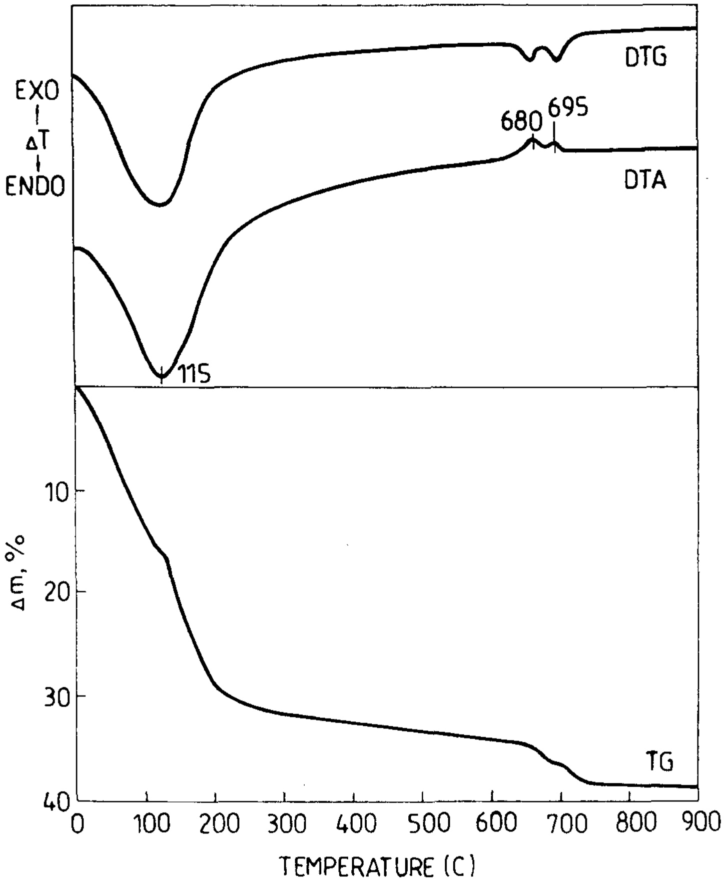

Fig. 1 DTA, DTG and TG curves of $Ca_2[Ti_2(O_2)_4(OH)_4]·4H_2O$

Results and discussion

Table 1 presents DTA, TG and DTG data on the thermal dehydration and decomposition of $Ca_2[Ti_2(O_2)_4(OH)_4]\cdot 4H_2O$ and $Sr_2[Ti_2(O_2)_4(OH)_4]\cdot 3H_2O$.

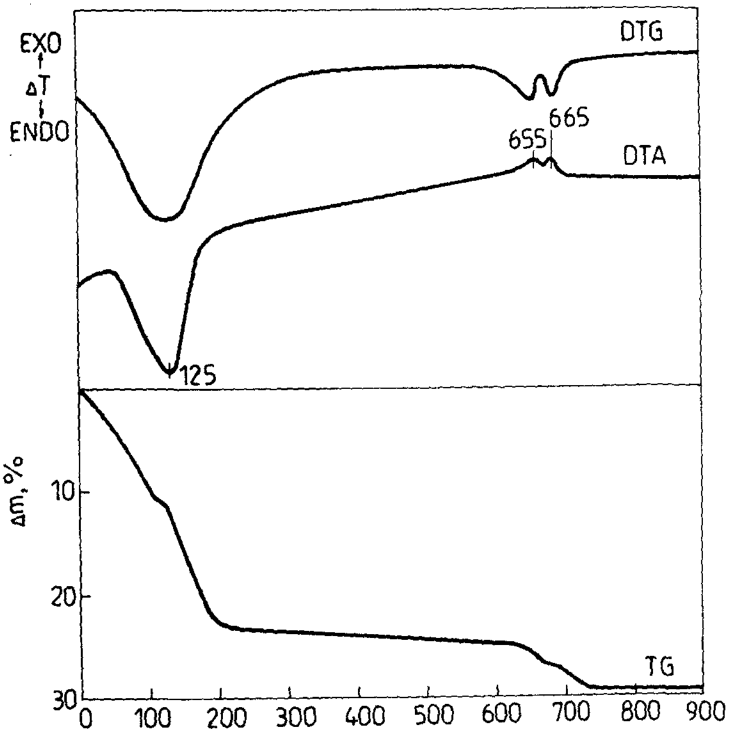

Fig. 2 DTA, DTG and TG curves of $Sr_2[Ti_2(O_2)_4(OH)_4]\cdot 3H_2O$

Isothermal investigations were undertaken with the aim of providing a more detailed interpretation of the thermal decomposition. Samples of these compounds were heated to constant weight at the most characteristic temperatures revealed by DTA: 130, 250, 420 and 680°C for calcium peroxotitanate, and 140, 210, 390 and 650°C for strontium peroxotitanate. The data from quantitative analysis of the intermediates are presented in Tables 2 and 3.

IR spectra were taken of the starting compounds and intermediates. Since they were analogous for the two compounds, Fig. 4 presents only those for calcium peroxotitanate. The final products were also investigated by X-ray phase analysis, the data being presented in diagrams showing the interplanar distances in Fig. 5.

Table 1 DTA, DTG and TG data on $Ca_2[Ti_2(O_2)_4(OH)_4]\cdot 4H_2O$ and $Sr_2[Ti_2(O_2)_4(OH)_4]\cdot 3H_2O$

Reactions			Δm / %		T_{max} /	Phase transition
			exp.	calc.	°C	ΔH°
$Ca_2[Ti_2(O_2)_4(OH)_4]\cdot 4H_2O$	→	$Ca_2[Ti_2(O_2)_4(OH)_4]+4H_2O$	15.6	16.2	115	$\Delta H^\circ > 0$
$Ca_2[Ti_2(O_2)_4(OH)_4]$	→	$Ca_2[Ti_2O_4(OH)_4]+2O_2$	14.3	14.4	220	$\Delta H^\circ > 0$
$Ca_2[Ti_2O_4(OH)_4]$	→	$2CaTiO_3+2H_2O$	8.8	8.1	680, 695	$\Delta H^\circ < 0$
$Sr_2[Ti_2(O_2)_4(OH)_4]\cdot 3H_2O$	→	$Sr_2[Ti_2(O_2)_4(OH)_4]+3H_2O$	10.1	10.7	125	$\Delta H^\circ > 0$
$Sr_2[Ti_2(O_2)_4(OH)_4]$	→	$Sr_2[Ti_2O_4(OH)_4]+2O_2$	11.8	12.3	195	$\Delta H^\circ > 0$
$Sr_2[Ti_2O_4(OH)_4]$	→	$2SrTiO_3+2H_2O$	7.6	6.9	655, 665	$\Delta H^\circ < 0$

Table 2 Intermediates from the thermal decomposition of $Ca_2[Ti_2(O_2)_4(OH)_4]\cdot 4H_2O$

T /	Quantitative analysis results / %					Ratio					Δ*m* / %	
°C	Ca	Ti	O_2	OH^-	H_2O	Ca	: Ti	: O_2	: OH^-	: H_2O	exp.	calc.
20	17.8	22.2	28.8	15.1	15.6	1.00	: 1.05	: 2.04	: 2.02	: 1.97	–	–
130	21.3	26.7	34.6	18.2	0.2	1.00	: 1.05	: 2.04	: 2.02	: 0.02	15.8	16.2
250	25.7	32.2	0.5	22.1	–	1.00	: 1.05	: 0.02	: 2.03	: –	14.2	14.4
420	25.8	32.2	–	22.0	–	1.00	: 1.05	: –	: 2.02	: –	0.3	–
680	28.5	35.8	–	0.1	–	1.00	: 1.05	: –	: 0.01	: –	8.3	8.1

Table 3 Intermediates from the thermal decomposition of $Sr_2[Ti_2(O_2)_4(OH)_4]\cdot 3H_2O$

T /	Quantitative analysis results / %					Ratio					Δ*m* / %	
°C	Sr	Ti	O_2	OH^-	H_2O	Sr	: Ti	: O_2	: OH^-	: H_2O	exp.	calc.
20	32.5	18.8	24.6	12.9	10.24	1.00	: 1.06	: 2.08	: 2.05	: 1.54	–	–
140	37.1	21.4	27.9	14.6	0.4	1.00	: 1.06	: 2.08	: 2.04	: 0.01	10.3	10.7
210	43.2	24.8	0.3	17.2	–	1.00	: 1.06	: 0.02	: 2.06	: –	12.1	12.3
390	43.4	24.8	–	17.1	–	1.00	: 1.06	: –	: 2.05	: –	0.2	–
650	46.9	26.8	–	0.1	–	1.00	: 1.05	: –	: 0.01	: –	7.0	6.9

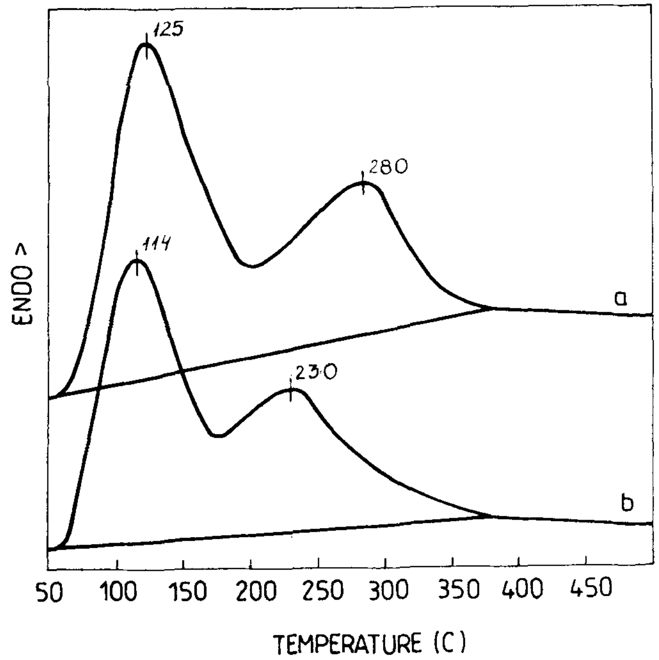

Fig. 3 DSC curves of: (a) $Ca_2[Ti_2(O_2)_4(OH)_4]\cdot 4H_2O$ and (b) $Sr_2[Ti_2(O_2)_4(OH)_4]\cdot 3H_2O$

The data in Table 1 reveal the analogous course of the respective DTA curves (Figs 1 and 2). They differ, albeit inessentially, in the temperatures at which the phase transitions of the corresponding compounds take place. The character of the latter is confirmed to a high degree by the IR spectra (Fig. 4).

According to the diagram, the strong endo effect observed with $T_{max}=115°C$ for calcium peroxotitanates and $T_{max}=125°C$ for strontium peroxotitanates corresponds to two processes which cannot be differentiated by means of DTA, whereas this is possible with DTG and TG. These two processes correspond to dehydration and decomposition of the peroxo compound, involving the release of oxygen. Evidence that the dehydration process takes place first is the change in mass (Δm) recorded from the TG curves, and the IR spectrum of the calcium peroxotitanate at 130°C (Fig. 4b). This latter spectrum, when compared with the IR spectrum of the initial sample, clearly shows the difference in the intensities of the absorption bands of the stretching vibrations of the hydrate water, and also the absence of the band of its bending vibration. The absorption band characteristic of the peroxide group $\mathrm{Ti}<\begin{smallmatrix}O\\|\\O\end{smallmatrix}$ is to be found at 875 cm^{-1} in the same spectrum. The second process, that of decomposition of the peroxide compounds and the release of O_2, as indicated by the course of the TG curves, takes place at a relatively low rate. The indicated processes are clearly differentiated in the DSC curves of both compounds, due to the high resolution capacity of the method. Corresponding to them are two endo effects, which merge into one another (Fig. 3). This renders accurate recording of ΔH^0 separately for dehydration and for decomposition difficult. The phase transition corresponding to the decomposition of the peroxide compound is readily proved by the IR spectrum of the sample heated at 420°C (Fig. 4c). The absorption band at 875 cm^{-1}, ascribed to the $\mathrm{Ti}<\overset{\mathrm{O}}{\underset{\mathrm{O}}{|}}$ group [9, 10], is no longer present (Tables 2 and 3).

Another vibration of this group appears in the region 500–650 cm^{-1} [9], which also contains the stretching vibrations of the Ti–O bonds. This is the reason for the obviously greater width of the absorption band in that region for the IR spectra of the initial compound and the sample heated at 130°C (Fig. 4b), as compared with that at 420°C (Fig. 4c). An exo effect appears at T_{max}=680 and 695°C for $Ca_2[Ti_2O_4(OH)_4]$ and at T_{max}=655 and 665°C for $Sr_2[Ti_2O_4(OH)_4]$, which is split to a considerable extent. According to this, the respective DTG curves contain two effects corresponding to the changes in the TG curves, corresponding to the decomposition of the intermediate to the simple titanate: $CaTiO_3$ and $SrTiO_3$, respectively. The characters of the exo effects

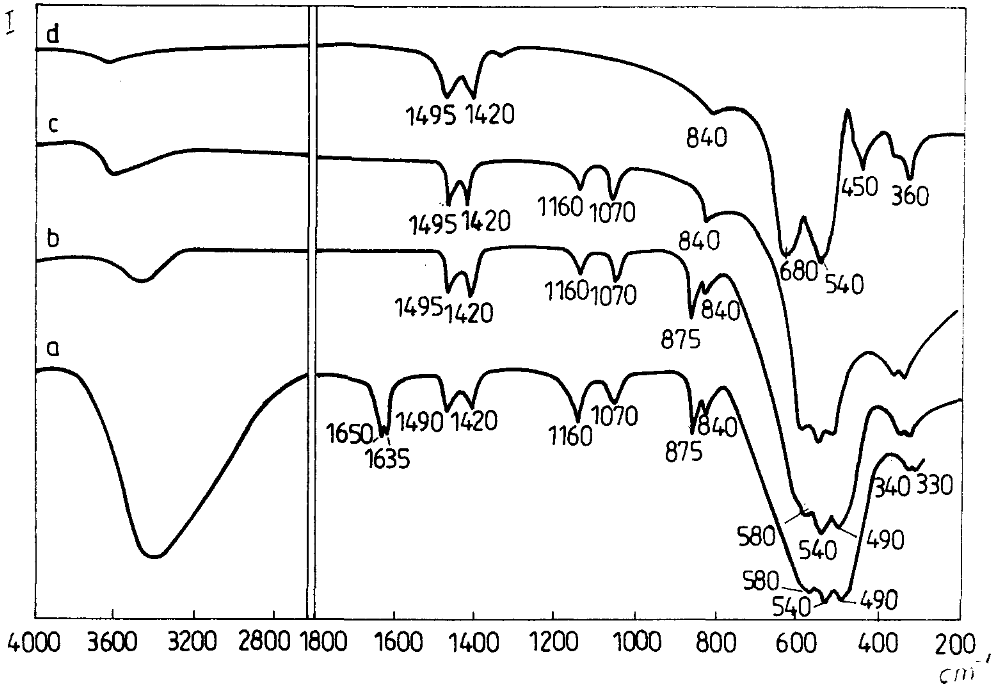

Fig. 4 IR spectra of: (a) $Ca_2[Ti_2(O_2)_4(OH)_4]\cdot 4H_2O$; (b) sample heated to 130°C; (c) sample heated to 420°C; and (d) sample heated to 680°C $CaTiO_3$

and of the TG curve can be explained in terms of the stepwise restructuralization of the compound and the release of the constitutionally bound water. The existence of metatitanates obtained was readily proved both by the Δm recorded in the TG curve and by the corresponding IR spectra (Fig. 4d). The absorption bands of the Ti–OH groups at 1160 and 1070 cm^{-1} were absent [11] and new bands corresponding to $CaTiO_3$ developed [12, 13]. The character of this transition is also in agreement with the data from the quantitative analysis of a sample heated at 680°C.

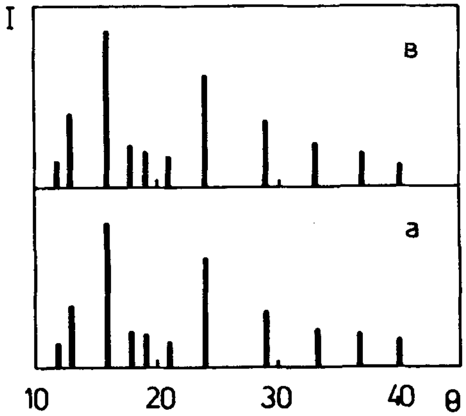

Fig. 5 Diagrams showing the interplanar distances of $CaTiO_3$; (a) $Ca_2[Ti_2(O_2)_4(OH)_4]\cdot 4H_2O$ heated to 680°C and (b) $Ca_2[Ti_2(O_2)_4(OH)_4]\cdot 4H_2O$ heated to 730°C

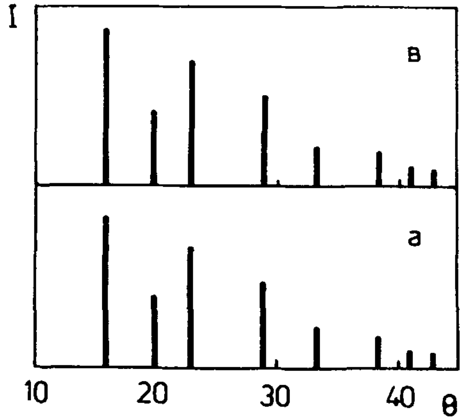

Fig. 6 Diagrams showing the interplanar distances of $SrTiO_3$; (a) $Sr_2[Ti_2(O_2)_4(OH)_4]\cdot 3H_2O$ heated to 650°C and (b) $Sr_2[Ti_2(O_2)_4(OH)_4]\cdot 3H_2O$ heated to 700°C

It is noteworthy, however, that the final samples from DTA taken at the same temperatures and corresponding to the respective metatitanates are amorphous, whereas the starting compounds heated to constant weight under the same conditions are evidently crystalline and the recorded effects correspond fully to the literature data for $CaTiO_3$ and $SrTiO_3$ [14] (Figs 5 and 6). This can be explained mainly by the different rates of the tempering process, assisting the crystallization of the substance. Samples heated to higher temperatures (730°C for calcium peroxotitanate and 700°C for strontium peroxotitanate) show an analogous diffractogram (Fig. 5). This was taken into consideration when planning the technology for producing $CaTiO_3$ and $SrTiO_3$.

The basis of this technology contains the schemes for the thermal decompositions of the initial peroxotitanates and metatitanates at optimum defined temperatures of 680°C for $CaTiO_3$ and 650°C for $SrTiO_3$, much lower than those in the dry methods. The resulting metatitanates possess qualities which make them applicable in the electronics industry.

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Zusammenfassung — Mittels DTA, TG, Röntgen-Phasenanalyse und IR-Spektroskopie wurde die thermische Dehydratation und Zersetzung von Ca^{2+} und Sr^{2+} Peroxotitanaten zu den entsprechenden Metatitanaten untersucht. Die Schritte des des Prozesses wurde ermittelt und die intermediären Phasen bestimmt. Die erhaltenen Informationen wurden zur Bestimmung der optimalen Temperatur benutzt, bei der die ursprünglichen Peroxotitanate erhitzt werden müssen, um eine Umwandlung zu Metatitanaten mit einem sehr hohen Kristallinitätsgrad zu erhalten (die optimale Temperatur für $CaTiO_3$ beträgt 680°C, für $SrTiO_3$ hingegen 650°C).