Journal of Thermal Analysis and Calorimetry, Vol. 84 (2006) 3, 589–592

THERMAL DECOMPOSITION OF CADMIUM PEROXOTITANATE TO $CdTiO_3$

V. Parvanova[*]

Department of Inorganic Chemistry, University of Chemical Technology and Metallurgy
8 Kliment Ohridski blvd., 1756 Sofia, Bulgaria

TG, DTA and DSC curves of $Cd_2[Ti_2(O_2)_2O(OH)_6]\cdot H_2O$ were recorded and used to determine the isothermal conditions suitable for obtaining the intermediate samples corresponding to the phases observed during the thermal decomposition. The samples were identified by quantitative analysis, IR spectroscopy and X-ray analysis. The experimental results were used to propose a mechanism of thermal decomposition of the investigated compound to $CdTiO_3$. The optimum conditions were also determined for obtaining $CdTiO_3$ with well-defined crystallinity.

Keywords: *cadmium peroxotitanate, $CdTiO_3$, DSC, simultaneous TG-DTA*

Introduction

The titanates have a broad application in electronics and this defines the great interest for their obtaining [1–4]. The cadmium titanate is used as solid solutions with other titanates in order to obtain thermal stability capacitors. It is presumed that $CdTiO_3$ determines a significant flattening of the maximum of the temperature dependence of the dielectric constant and dielectric losses are decreased.

$CdTiO_3$, with grain size under 1 μ, was obtained by thermal decomposition of $Cd_2[Ti_2(O_2)_2O(OH)_6]\cdot H_2O$ at T=600–650°C for 2–3 h. $Cd_2[Ti_2(O_2)_2O(OH)_6]\cdot H_2O$ was synthesized by peroxomethod [5]. This method from technological point of view exhibits some important advantages compared to the conventional methods for obtaining titanates: significantly lower temperature of synthesis, shorter reaction time, avoiding the milling and homogenizing of the raw materials and of the final product. As a result the obtained metatitanates are of higher purity, with fine crystalline structure and homogeneous grain-size composition.

The object of the present investigation is to obtain information about the mechanism of thermal decomposition of $Cd_2[Ti_2(O_2)_2O(OH)_6]\cdot H_2O$ to $CdTiO_3$. For this purpose the following methods are used: simultaneous TG-DTA, DSC, X-ray analysis, IR-spectrum and quantitative analysis. The optimum conditions are determined for the obtaining of $CdTiO_3$.

Experimental

The cadmium peroxotitanate is obtained by the peroxomethod [6, 7] and its synthesis can be expressed by the following reaction:

$$TiCl_4+Cd(CH_3COO)_2+H_2O_2+OH^- \rightarrow$$
$$\rightarrow Cd_2[Ti_2(O_2)_2O(OH)_6]\cdot H_2O$$

0.1 M water solution of $Cd(CH_3COO)_2$ is added to 0.1 M $TiCl_4$ solution in HCl. A five-time excess of H_2O_2 is also added. After cooling the mixture, diluted solution of NH_3 is added until obtaining pH=9. During the reaction the temperature is kept at about 10°C. A pale yellow amorphous sediment of $Cd_2[Ti_2(O_2)_2O(OH)_6]\cdot H_2O$ is obtained. After its calcination in air atmosphere, $CdTiO_3$ is obtained.

The thermal decomposition of $Cd_2[Ti_2(O_2)_2O(OH)_6]\cdot H_2O$ is studied by simultaneous TG-DTA and DSC methods. The derivatograph investigations were recorded on a MOM-OD-102 apparatus in the temperature range of 20–900°C in air at heating rate of 10°C min^{-1} and a mass sample of 25 mg.

For more accurate proof of the mechanism of the thermal decomposition, isothermal investigations were also performed. Based on DTA data, the temperatures of thermal treatment of 2 g samples were determined (T=100, 370, 550°C). The enthalpy changes accompanying the decomposition were measured. The DSC curves were recorded on a Perkin Elmer DSC-4 apparatus in the temperature range 20–450°C, at a heating rate of 10°C and a mass sample of 4.2 mg.

The stoichiometry composition of the compounds was determined by using the following methods of analysis: Ti^{4+} by gravimetric method [8], Cd^{2+} by complexometric method [9], the peroxo groups by permanganometric method [10], hydroxyl groups by Chernev's method [11] and water by Fisher's method [12].

The IR spectra were recorded on a Philips PV 9700 spectrograph in the 4000 to 650 cm^{-1} in KBr pellets and, in the region of stretching vibrations of H_2O, as a suspension in hexachloro-1,3-butadiene.

---

[*] vparvanova@hotmail.com

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

The final product, $CdTiO_3$, was characterized by X-ray diffraction using a Zeiss TUR-M-62 apparatus with CuK_α radiation.

Results and discussion

The IR-spectrum of the studied compound at T=20°C is presented in Fig. 1. DTA and TG curves are shown on Fig. 2, IR-spectra of the intermediate samples obtained by isothermal calcination – Fig. 3 and DSC curve – Fig. 4. Table 1 presents quantitative analysis data of the starting compound and isothermally treated compound at different selected temperatures. Table 2 contains values of the mass changes and the corresponding temperature ranges of the recorded stages in the derivatogram and DSC plot.

The composition of the cadmium peroxotitanate used as a precursor for obtaining of $CdTiO_3$ was determined by quantitative analysis and is presented in Table 1 (data at T=20°C). The composition is also confirmed by its IR-spectrum (Fig. 1). In the IR-spectrum stretching vibrations $\nu_{Ti–O}$ at 765, 740 and 670 cm^{-1} [13] and for peroxo groups at 880 cm^{-1} [14, 15] are observed. The weak absorption bands at 1080 and 1150 cm^{-1}, which correspond to $\delta_{Ti–OH}$ terminal groups and $\delta_{Ti–O(H)–Ti}$ bridging groups [13] are of interest. The last mentioned groups define the binuclear complex. The strong absorption band at 1380 cm^{-1} confirms the binuclear structure [16]. The OH^- absorption bands at 3280, 3420 and 3530 cm^{-1} define the presence of three types of OH^- groups: hydrate water, terminal and bridging OH^-. The complete identification is impossible because of the absence of structure data, which could give information about the types of hydrogen bands participating in these groups. The presence of OH^- groups bellowing to the hydration water is proved by δ_{H_2O} absorption band at 1630 cm^{-1}.

The DTA curve (Fig. 2) of the $Cd_2[Ti_2(O_2)_2O(OH)_6]\cdot H_2O$ shows that its decomposition starts at 45°C. The first endothermal effect is studied in the 45–250°C range with T_{max}=123°C. To this effect, on the TG curve, a mass change Δm=9.8% corresponds, related to the release of hydration water and O_2 during the decomposition of the peroxo groups. This statement is also proved by the quantitative analyses data of the isothermal treated compound at T=100°C which shows a good correlation between Δm=9.3% for Δm_{calcd}=9.6% (Table 1). From the comparison between the IR-spectra of the starting compound (Fig. 3a) and those of the isothermal treated sample at 100°C (Fig. 3b), a lack of absorption bands at 1630 and 880 cm^{-1} is observed. This is another proof that up to this temperature hydration water and O_2 of the peroxo groups dissociate totally.

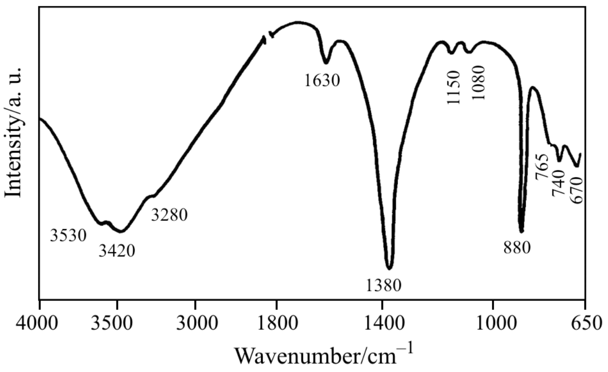

Fig. 1 IR spectrum of $Cd_2[Ti_2(O_2)_2O(OH)_6]\cdot H_2O$

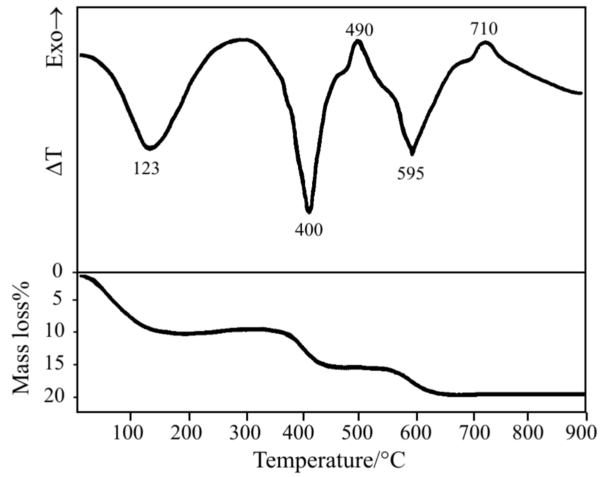

Fig. 2 DTA and TG curves of $Cd_2[Ti_2(O_2)_2O(OH)_6]\cdot H_2O$

Two effects are observed on the DSC curve for the discussed area (Fig. 4). The first one is an endothermal effect with T_{max}=120°C and ΔH^0=+128±1.0 kJ mol^{-1}

Table 1 Quantitative analyses data of the starting compound $Cd_2[Ti_2(O_2)_2O(OH)_6]\cdot H_2O$ and isothermal treated compound at selected temperatures

Temperature/°C	Quantitative composition/mass%					Mol ratio	Δm/%	
	Cd^{2+}	Ti^{4+}	O_2^{2-}	OH^-	H_2O	$Cd:Ti:O_2^{2-}:OH^-:H_2O$	exp.	calcd.
20	42.5	18.3	12.2	19.0	3.5	1.00:1.00:1.00:2.95:0.51	–	–
100	47.2	20.6	–	22.0	–	1.00:1.02:–:3.08:–	9.3	9.6
370	51.2	22.3	–	7.6	–	1.00:1.02:–:0.98:–	7.3	6.9
550	53.5	23.2	–	–	–	1.00:1.02:–:–:–	3.4	3.5

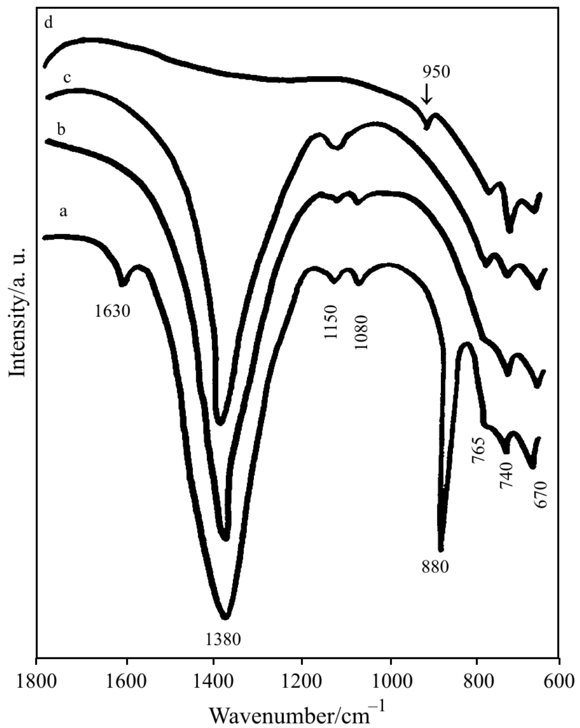

Fig. 3 IR spectra of: a – $Cd_2[Ti_2(O_2)_2O(OH)_6]\cdot H_2O$ at T=20°C; b – isothermal treated sample at T=100°C; c – heated sample at T=370°C; d – heated sample at T=550°C

and the second one is exothermal effect with T_{max}=217°C and ΔH^0=–19±0.1 kJ mol^{-1} (Table 2). The last effect is possibly due to the structural changes in the $Cd[Ti_2O_3(OH)_6]$ complex formation process and probably of the summing effects is not recorded on the DTA curve. The absence of the second endothermal effect in the discussed temperature range proves that the release of the hydration H_2O and O_2 takes place at the same time.

The second observed endothermal effect on the DTA curve in the 357–460°C range with T_{max}=400°C may due to the dissociation of the H_2O during the separation of the terminal OH-groups.To this effect, on the TG-curve to mass loss – Δm=6.6% corresponds, in good agreement with $\Delta m_{calcd.}$=6.9% and with the mass loss of the isothermal treated sample at T=370°C, Δm=7.3%. The quantitative analysis shows decrease of the OH^--groups from 3.08 to 0.98 mol (Table 1). In the IR-spectrum of the same sample the absorption band at 1080 cm^{-1}, which is typical for δ_{OH^-} of terminal T–OH groups is absent (Fig. 3c). The endothermal effect with T_{max}=395°C on the DSC curve corresponds to the process of separation of the OH^- groups (Fig. 4). The enthalpy of this phase transition is ΔH^0=78±0.5 kJ mol^{-1} (Table 2).

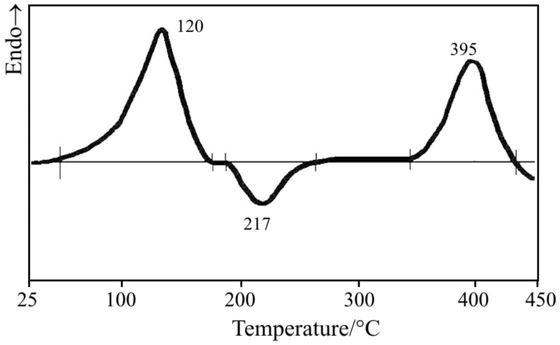

Fig. 4 DSC curve of $Cd_2[Ti_2(O_2)_2O(OH)_6]\cdot H_2O$

A weak exothermal effect is observed on the DTA curve at T=490°C (Fig. 1), which is not correlated with a mass loss on the TG curve. This exothermal effect is probably a result of the formation of the complex $Cd_2[Ti_2O_5(OH)_2]$.

Temperature range 560–655°C with T_{max}=595°C on the DTA third endothermal effect is recorded with a corresponding Δm=3.7%. This effect is a result of the process of elimination of the bridging OH-groups from Ti–O(H)–Ti. The IR-spectrum of the isothermal treated sample at T=550°C shows a lack of absorption bands of δ_{OH}^- of the bridging Ti–O(H)–Ti at 1150 and 1380 cm^{-1} (Fig. 3d). Table 1 shows for the isothermal treated sample at T=550°C a mass change Δm=3.4% compared to $\Delta m_{calcd.}$=3.5%. At this temperature the quantitative analysis data shows the total release of OH^- groups, the final composition corresponding to $CdTiO_3$ (Table 1). However, the X-ray analysis of this sample evidences an amorphous character of the sample.

The weak exothermal effect at T=710°C on DTA curve is not correlated with a mass change on the TG curve. This effect is probably due to the structural changes, which lead to the formation of $CdTiO_3$. The X-ray analysis of the DTA residue shows an amor-

Table 2 DTA, TG and DSC data of $Cd_2[Ti_2(O_2)_2O(OH)_6]\cdot H_2O$ decomposition

Temperature range/°C	DTA		DSC		Δm/%	
	T_{max}/°C	T_{onset}/°C	T_{max}/°C	ΔH^0/kJ mol^{-1}	exp.	calcd.
45–250	123	79	120	128±1.0	9.8	9.6
–	–	193	217	–19±0.1	–	–
357–460	400	357	395	78±0.5	6.6	6.9
470–520	490	–	–	<0	–	–
560–655	595	–	–	0>	3.7	3.5
685–750	710	–	–	<0	–	–

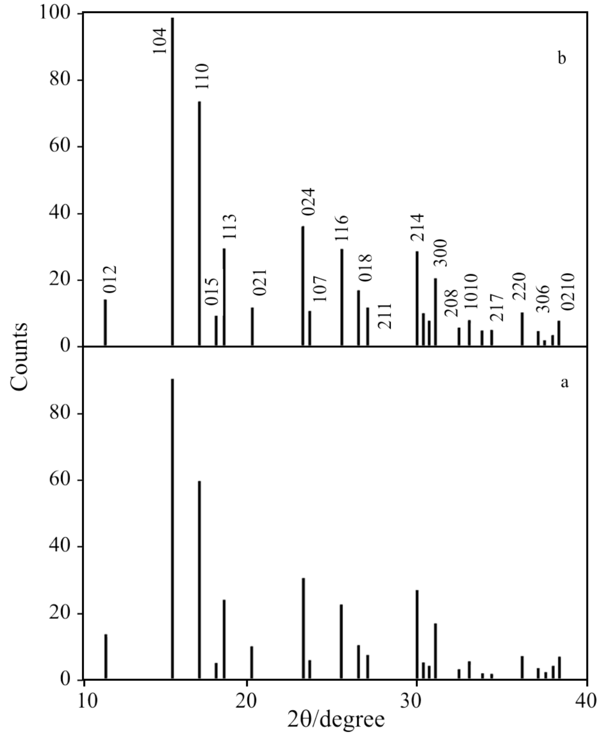

Fig. 5 Schematic diagram of the X-ray diffraction lines for $CdTiO_3$ obtained at: a – 600°C for 3 h; b – 650°C for 2 h

phous phase because of the high heating rate of 10°C min^{-1}. On the contrary, the isothermal treated sample at T=700°C calcinated for 1 h is crystalline and has the diffraction patterns on $CdTiO_3$ [17].

On the basis of DTA, TG and DSC, quantitative composition and IR-spectra data, the following mechanism of the thermal decomposition of $Cd_2[Ti_2(O_2)_2O(OH)_6]\cdot H_2O$ to $CdTiO_3$: can be proposed:

$$Cd_2[Ti_2(O_2)_2O(OH)_6]\cdot H_2O_{(s)} \xrightarrow{45-250^\circ C}$$

$$Cd_2[Ti_2O_3(OH)_6]_{(s)}+H_2O_{(g)}+O_{2(g)}$$

$$Cd_2[Ti_2O_3(OH)_6]_{(s)} \xrightarrow{357-460^\circ C}$$

$$Cd_2[Ti_2O_5(OH)_2]_{(s)}+2H_2O_{(g)}$$

$$Cd_2[Ti_2O_5(OH)_2]_{(s)} \xrightarrow{560-655^\circ C} 2CdTiO_{3(s)} + H_2O_{(g)}$$

The optimum conditions of calcination are interesting to be studied in order to obtain $CdTiO_3$ with good crystallinity. Samples with a mass of 5 g have been calcinated at T=700, 650, 600 and 550°C for 1, 2, 3 and 4 h in air. The optimum results have been obtained at T=600°C for 3 h and at T=650°C for 2 h (Fig. 5).

Conclusions

$Cd_2[Ti_2(O_2)_2O(OH)_6]\cdot H_2O$, which a precursor for obtaining $CdTiO_3$, was synthesized by peroxomethod.

On the basis of the DTA, DSC, IR-spectroscopy, quantitative and X-ray analysis data, a mechanism for the thermal decomposition of $Cd_2[Ti_2(O_2)_2O(OH)_6]\cdot H_2O$ to $CdTiO_3$ has been proposed.

The optimum conditions for obtaining $CdTiO_3$ with a good crystallinity degree are the thermal treatments of $Cd_2[Ti_2(O_2)_2O(OH)_6]\cdot H_2O$ in air at 600°C for 3 h, or at 650°C for 2 h.

References

1 A. Ianculescu, A. Brăileanu, M Zaharescu, S. Guillemet, I. Pasuk, J. Madarász and G. Pokol, J. Therm. Anal. Cal., 72 (2003) 173.
2 G. Colon, M. A. Aviles, J. A. Navio and P. J. Sanchez-Soto, J. Therm. Anal. Cal., 67 (2002) 229.
3 M. Moran-Pineda, S. Castillo, M. Asomoza and R. Gomez, J. Therm. Anal. Cal., 73 (2003) 341.
4 C. E. F. Costa, S. C. L. Crispim, S. J. G. Lima, C. A. Paskocimas, E. Longo, V. J. Fernandes, A. S. Araujo and I. M. G. Santos, J. Therm. Anal. Cal., 75 (2004) 467.
5 Pat. Jap. 51-80 Cl. C 01 G 23/00.
6 M. Maneva and V. Parvanova, J. Thermal Anal., 44 (1995) 353.
7 V. Parvanova and M. Maneva, Thermochim. Acta, 279 (1996) 137.
8 Charlot, Methods of Analytical Chemistry, Quantitative Analysis of Inorganic Compounds, Himia, Moscow 1965, p. 827 (in Russian).
9 Komplexometrische Bestimmungsmethode mit Titriplex, E. Merck AG, Darmstadt 1972.
10 B. Zagorchev, Analit. Chimia, Technika, Sofia 1972, p. 564 (in Bulgarian).
11 B. Chernov, Collection of Natural Soil Activity, ANSSSR, Moscow 1947, p. 41 (in Russian).
12 D. Mitchel and D. Smith, Aquametry, Himia, Moscow 1980, p. 35 (in Russian).
13 K. Nakamoto, IR Spectra of Inorganic and Coordination Compounds, 2^{nd} Ed., Moscow 1969, p. 89 (in Russian).
14 W. Griffith, J. Chem. Soc., 12 (1964) 5248.
15 G. Jere and C. Pater, Can. J. Chem., 40 (1962) 1556.
16 R. Barabanchikova, T. Limar and M. Mochossoev, Collection of Inorganic Peroxide Compounds, Nauka, Moscow 1975, p. 130 (in Russian).
17 JCPDS-29-0277.

Received: July 25, 2005
Accepted: November 9, 2005

DOI: 10.1007/s10973-005-7022-z