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THERMAL DECOMPOSITION OF NICKEL AND ZINC PEROXOTITANATES TO METATITANATES

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Abstract

Methods of DTA, TG, X-ray phase analysis and IR spectroscopy were used to study the thermal dehydration and decomposition of Ni^{2+} and Zn^{2+} peroxotitanates to the corresponding metatitanates. The course of the process was established and the intermediate phases were identified. The information obtained was utilized to determine the optimum temperatures of heating the initial peroxotitanates for conversion to metatitanates with a fairly high degree of crystallinity (for $ZnTiO_3$ the optimum temperature is 600°C, while for $NiTiO_3$ it is 550°C).

Keywords: DTA-TG, IR, Ni and Zn peroxotitanates, X-ray

Introduction

Nickel and zinc metatitanates possess valuable electrophysical properties, which accounts for the interest in these compounds. Information has been published on methods of obtaining them. According to [1–3], the metatitanates $NiTiO_3$ and $ZnTiO_3$ are obtained from the appropriate oxides NiO or ZnO and TiO_2 by heating to 1350–1380°C and to 750–800°C, respectively. Another publication [4] suggests the use of tartaric acid, hydrated TiO_2 and hydrated NiO or ZnO as starting compounds, taken in stoichiometric proportions, mixed in aqueous solutions at about the boiling point. A precipitate of undetermined composition is formed upon the addition of C_2H_8OH. When this is heated to over 600°C, $NiTiO_3$ is obtained. $ZnTiO_3$ may be obtained in a fine crystalline state at 600°C. There is also information on the synthesis of $NiTiO_3$ by treating Li_2TiO_3 with $NiCl_2$ and KCl for 48 h at 700°C [5], and on $ZnTiO_3$ formation from tetrabutyltitanate with ZnO or ZnC_2O_4 in aqueous medium, the initial precipitate being heated [6, 7]. In [8] we determined the optimum conditions for obtaining Ni^{2+} and Zn^{2+} peroxotitanates by a method analogous to that described in [9], and we also established the quantitative compositions of these compounds:

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$$Ni_2[Ti_2(O_2)_2(OH)_8]\cdot 4H_2O \text{ and } Zn_2[Ti_2O_2(O_2)_2(OH)_4]\cdot 2H_2O$$

The aim of the present study was to use methods of DTA, TG and DTG, X-ray analysis and IR spectroscopy to obtain information on the chemistry and thermal decompositions of $Ni_2[Ti_2(O_2)_2(OH)_8]\cdot 4H_2O$ and $Zn_2[Ti_2O_2(O_2)_2(OH)_4]\cdot 2H_2O$, and hence on the molecular structures of the starting and intermediate compounds.

Experimental

The stoichiometry of the investigated compounds was determined by using the following methods of analysis: titanium gravimetrically [10]; nickel and zinc complexometrically [11]; peroxide permanganometrically [12]; hydroxy groups by Chernov's method [13]; and water by Fischer's method [14]. The thermoanalytical curves of the starting and intermediate samples were measured with Perkin-Elmer equipment at a heating rate of 10 deg$\cdot$min^{-1} up to 750°C for nickel peroxotitanate, and up to 700°C for zinc peroxotitanate. The IR spectra were taken in KBr tablets with a Zeiss IR-70 spectrophotometer (4000 to 400 cm^{-1}). In the region of the water stretching vibrations, the spectra were taken of suspensions in hexachloro-1,3-butadiene. The X-ray phase examination data were obtained with Zeiss TUR-M-62 equipment during CuK_α irradiation.

Results

The DTA, DTG and TG curves of $Ni_2[Ti_2(O_2)_2(OH)_8]\cdot 4H_2O$ and shown in Fig. 1. On the basis of these data it is difficult to identify the consecutive stages of the process of thermal decomposition, since the course of the TG curve makes it difficult to differentiate the Δm corresponding to the DTA endo and exo effects, namely at $T_{max}=140$°C (endo) and $T_{max}=315$°C (exo). After these processes, the course of the TG curve shows no mass loss. The IR spectrum of the sample heated in DTA to 400°C corresponds to that of $NiTiO_3$ (Fig. 3b), i.e. it shows no absorption bands of the peroxide group (860 cm^{-1}) or of bridging OH groups (1150 cm^{-1}), characteristic of the starting nickel peroxotitanate. Instead, broad absorption band of the Ti–O bonds appeared, with typical semi-width due to the amorphous nature of the product (Fig. 3b). The diffractogram of the same sample confirmed this.

In view of the compositions of the starting compound and the final product ($NiTiO_3$), it follows that overall the stoichiometry of the thermal decomposition may be described by a chemical equation of the type:

$$Ni_2[Ti_2(O_2)_2(OH)_8]\cdot 4H_2O = 2NiTiO_3+8H_2O+O_2$$

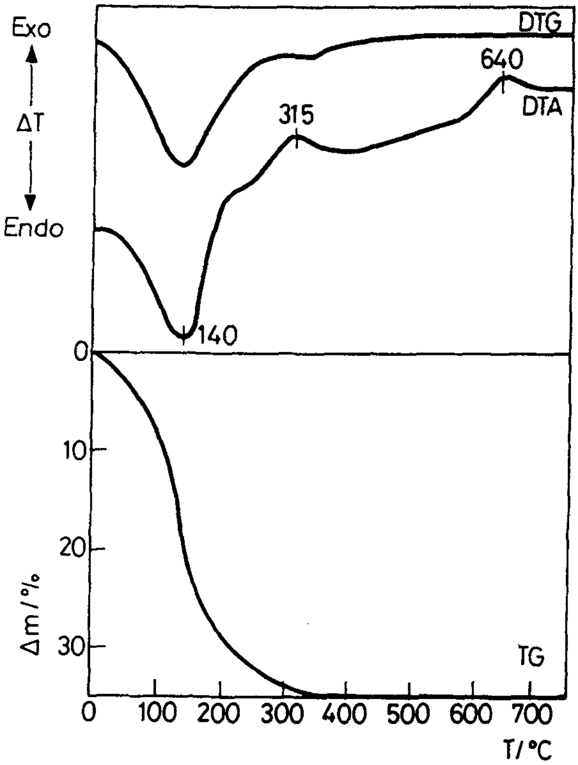


Fig. 1 DTA, DTG, TG of $Ni_2[Ti_2(O_2)_2(OH)_8]\cdot4H_2O$

The DTA curve provides information that this phase transition corresponds to an endothermic process with T_{max} at 140°C and an exo process with T_{max} at 315°C. Compared with the effects observed for the alkaline earth peroxotitanates [15], these phenomena indicate that the endo effect corresponds to the release of hydrate water and O_2 from the peroxide groups, without any possibility of differentiating the two processes. In $Ni_2[Ti_2(O_2)_2(OH)_8]\cdot4H_2O$, after these effects an exo-effect proceeds. This is connected with release of hydroxy groups in the form of H_2O and with restructuralization until amorphous $NiTiO_3$ is obtained. This process takes place at lower temperature than for the alkaline earth peroxotitanates. The course of the TG curve prior to the formation of $NiTiO_3$ shows a gradual release of the structural water from the compound.

An other exo effect is to be observed in the DTA curve, at T_{max}=640°C, without any loss in mass from the sample. This is caused by a phase change involving crystallization of the initially obtained amorphous form of $NiTiO_3$. The DTA curves show that this exists in such a form in a definite temperature interval. This assumption agrees with the IR spectrum of the sample heated to 700°C

(Fig. 3c), the sample corresponding to $NiTiO_3$ [16]. The crystalline $NiTiO_3$ obtained was checked via its X-ray pattern (Fig. 5b). The sample was heated (to constant mass) to 540°C, with the aim of seeking the optimum temperature in the isothermal heating of the amorphous product to yield crystalline $NiTiO_3$. The diffractogram patterns exhibited better crystallinity than those of the sample after heating in DTA to 700°C.

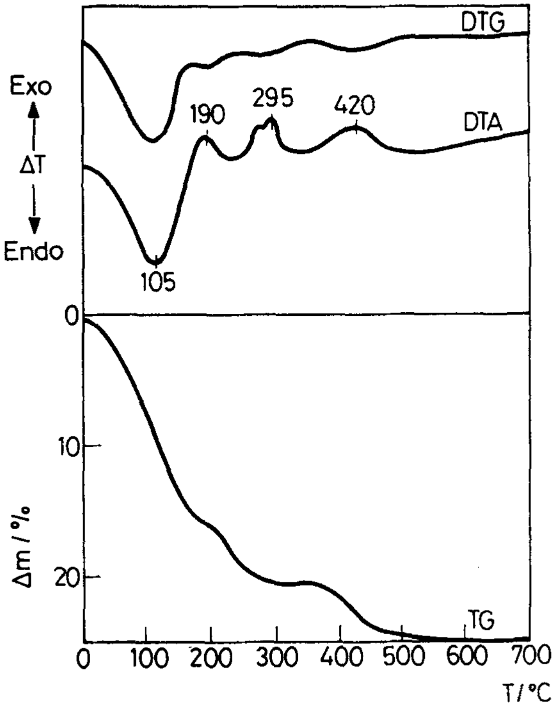


Fig. 2 DTA, DTG, TG of $Zn_2[Ti_2O_2(O_2)_2(OH)_4]\cdot 2H_2O$

The data from the DTA and TG curves for $Zn_2[Ti_2O_2(O_2)_2(OH)_4]\cdot 2H_2O$, unlike those for $Ni_2[Ti_2(O_2)_2(OH)_8]\cdot 4H_2O$, make it possible to differentiate between several partial processes of thermal decomposition, as shown in Table 1. These were determined mainly on the basis of the TG curve changes. Two intervals without Δm are clearly visible, the second one corresponding to a rather broad temperature interval. The data from the quantitative analysis (Table 2) and the IR spectra (Fig. 4) of samples heated to constant mass correspond to these two intervals.

According to the proposed schedule, the endo effect observed with maximum at 105°C is immediately transformed into a small exo-effect with T_{max} at 190°C. This corresponds to release of the water molecule from the external sphere and of the oxygen from the peroxide groups. From the TG curve, corresponding to these processes, it is found that Δm_{exp} 16% (Δm_{calc}=15.9%).

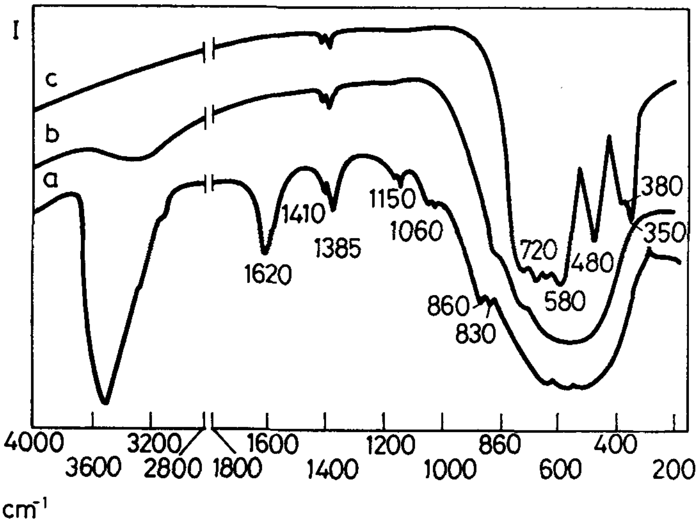


Fig. 3 IR spectra of: a) $Ni_2[Ti_2(O_2)_2(OH)_8]\cdot 4H_2O$; b) heated at 400°C; c) $NiTiO_3$ of heated sample to 550°C

Two exo effects may be observed in the DTA curve of $Zn_2[Ti_2O_2(O_2)_2(OH)_4]\cdot 2H_2O$, at T_{max}=295°C (slightly split) and at T_{max}=420°C. The former corresponds to the further dehydration of the compound at the expense of the hydroxy groups. It is accompanied by its restructuralization, leading to a more stable intermediate. This agrees with the interval without loss in mass in the TG curve. This process corresponds to a decrease in mass, Δm_{exp}=4.4% (Δm_{calc}=4.2%), i.e. the release of one molecule of water. It is confirmed by the IR spectrum of a sample heated to 350°C (Table 2, Figs 4–b).

The exo effect with maximum at 420°C is due to release of the last water molecule, probably from the bridging OH groups, and formation of the thermodynamically stable $ZnTiO_3$. No other effect is to be observed in the DTA curve until the end (T=700°C), and this justifies the assumption that, at the heating rate applied (10 deg·min^{-1}), the end-product obtained ($ZnTiO_3$) is amorphous. This assumption is confirmed by the diffractogram, which does not show the effects characteristic of $ZnTiO_3$. However, a sample of starting zinc peroxotitanate heated to constant weight at 600°C shows the effects presented in [17].

The proposed diagram of thermal decomposition correlates well with the data in Table 2 and Fig. 4. Additional information is obtained on the molecular structure of the initial $Zn_2[Ti_2O_2(O_2)_2(OH)_4]\cdot 2H_2O$ too. The IR spectra prove the presence of bridging OH groups (the absorption band at 1135 cm^{-1}), deter-

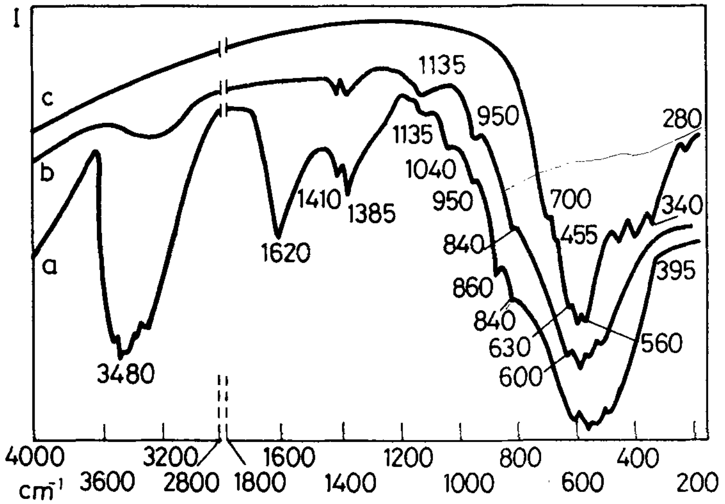


Fig. 4 IR spectra of: a) $Zn_2[Ti_2O_2(O_2)_2(OH)_4]\cdot 2H_2O$; b) heated to 350°C; c) heated sample to 600°C

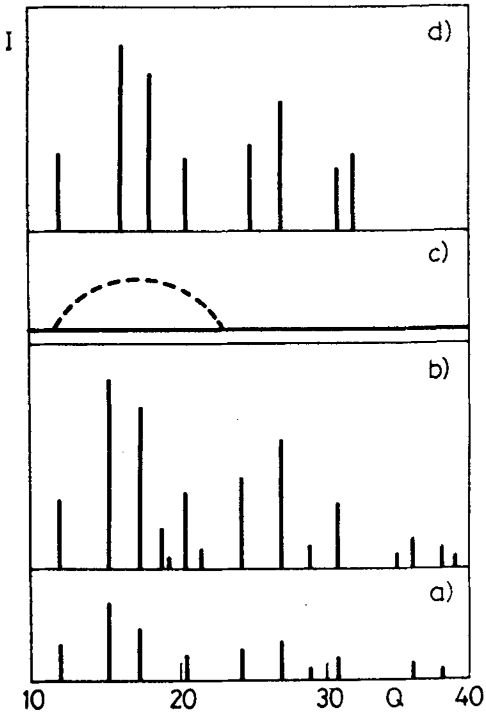


Fig. 5 Interplanar distance diagrams of: a) $NiTiO_3$ (from DTA) at T=700°C; b) $NiTiO_3$ of heated sample at T=550°C; c) $ZnTiO_3$ (from DTA) at T=700°C; d) $ZnTiO_3$ of heated sample at T=600°C

Table 1 DTA and TG information on $Zn_2[Ti_2O_2(O_2)_2(OH)_4]\cdot 2H_2O$

Phase transition	Δm / %		T_{max}	Phase transition
	exp	calc.	°C	H^o
$Zn_2[Ti_2O_2(O_2)_2(OH)_4]\cdot 2H_2O = Zn_2[Ti_2O_4(OH)_4] + 2H_2O + O_2$	16.0	15.9	105	$H^o > 0$
			190	$H^o < 0$
$Zn_2[Ti_2O_4(OH)_4] = Zn_2[Ti_2O_5(OH)_2] + H_2O$	4.4	4.2	295	$H^o < 0$
$Zn_2[Ti_2O_5(OH)_2] = 2ZnTiO_3 + H_2O$	4.3	4.2	420	$H^o < 0$

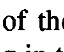
mining the presence of a binuclear complex, and the presence of Ti-OH groups with characteristic absorption at 1080 cm^{-1} [18]. Similarly, the presence of peroxide groups of the type  $\mathrm{Ti}\overset{O}{\underset{O}{}}$ is characterized by the absorption at 860 cm^{-1} and those lying in the region of the intense absorption band of the stretching vibrations of the Ti–O bond [19, 20] (Table 2, Fig. 4a). Unlike the spectra of $Ni_2[Ti_2(O_2)_2(OH)_8]\cdot4H_2O$ and the alkaline earth peroxotitanates [15], the presence of the –Ti=O groups is well demonstrated in the IR spectrum of $Zn_2[Ti_2(O_2)_2(OH)_4]\cdot2H_2O$. According to [19], this group is responsible for the absorption band at 950 cm^{-1}.

Table 2 Data from quantitative analysis of intermediates in thermal decomposition of $Zn_2\ [Ti_2O_2\ (O_2)_2\ (OH)_4]\cdot2H_2O$

T /	Composition/%					Ratio					Δm / %	
°C	Zn	Ti	O_2^{2-}	OH^-	H_2O	Zn :	Ti :	O_2^{2-} :	OH^- :	H_2O	exp.	calc.
20	30.2	23.4	15.0	15.8	7.9	1.00 :	1.06 :	1.02 :	2.02 :	0.96	–	–
200	35.6	27.5	0.6	18.6	0.3	1.00 :	1.06 :	0.03 :	2.03 :	0.03	16.2	15.9
350	37.7	28.9	–	9.9	–	1.00 :	1.06 :	–	1.02 :	–	4.3	4.2
600	39.8	30.9	–	–	–	1.00 :	1.06 :	–	–	–	4.4	4.2

The IR spectrum of the sample isolated in the region of the interval without change in mass, corresponding to the composition $Zn_2[Ti_2O_5(OH)_2]$, shows the presence of the bridging OH groups (1135 cm^{-1}), and also the absorption characterizing the –Ti=O groups, with higher intensity in this case (Table 2, Fig. 4b). The spectrum of the $ZnTiO_3$ obtained agrees with the literature data [16] (Fig. 4c).

An analysis of the experimental data demonstrates that the newly synthesized nickel and zinc peroxotitanates undergo a complex scheme of thermal decomposition, differing from the decompositions of analogous compounds [15], but the processes also lead to the formation of $NiTiO_3$ and $ZnTiO_3$.

References

1 B. Loshkarev, A. Sycheva and A. Ustyantseva, Izv. Acad. Nauk SSSR Neorg. Mater., 3, 11 (1967) 2040.

2 G. N. Vertuchkov, Mineral. Kristalogr. Tr. Soveshch. Meeting date., (1969) 208.

3 A. Scheinkman, F. Scheinkman, I. Dobrovolskii and G. Zvyagina, Izv. Akad. Nauk. SSSR, Neorg. Mater., 13 (8) (1977) 1447.

4 Y. Saikali and J. Paria, C. R. Acad. Sci. Paris, 265 (1967) Serie C. 1041.

5 B. Durand and J. Paria, C. R. Acad. Sci. Paris, 281 (1975) Serie C. 539.

6 Patent Japan No.50053300/ C01G (1975).

7 Patent Germany No.2214922/ C01G (1972).

8 M. Maneva, V. Parvanova and L., Genov, Annuaire de l'école suppérieure de Chimie Technologique. XXXI, 2 (1991) 10.

9 Patent Japan No.51-80C/C01G23/00 (1976).
10 G. Charlot Methods of Analytical Chemistry. Quantative Analysis of Inorganic Compounds, Chimia, Moskow 1965, p. 827, (in Russian).
11 E. AG. Merk, Komplexometrische Bestimmungsmethoden mit Titriplex, Darmstadt. 1972, pp. 45, 53.
12 B. Zagorchev, Analyt. Chim. Technica. Sofia, (1972) 564.
13 B. Chernov, Collection of Natural Soil Acidity A.N.SSSR Moskow 1947, p. 41.
14 J. Mitschell and D. Schmidt, Aquametry, Chimia, Moskow, 1980 p. 35.
15 L. Genov, M. Maneva and V. Parvanova, J. Thermal Anal., 33 (1988) 727.
16 E. Baran and I. Batto, Z. Anorg. Allg. Chem., 444 (1978) 282.
17 Davey kwic index, Materials Research Laboratory, 1979, p. 1259.
18 K. Nakamoto, IR-spectra of Inorganic and Coordination Compounds, 2nd Edition, Chimia, Moskow 1969 p. 89.
19 W. Griffith, J. Chem. Soc., (1964) 5248.
20 G. Jere and C. Patel, Canad. J. Chem., 40 (1962) 1376.

Zusammenfassung — Mittels DTA, TG, Röntgen-Phasenanalyse und IR-Spektroskopie wurde die thermische Dehydratation und Zersetzung von Ni^{2+} und Zn^{2+} Peroxotitanaten zu den entsprechenden Metatitanaten untersucht. Der Verlauf 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 $ZnTiO_3$ beträgt 600°C, für $NiTiO_3$ hingegen 550°C).