

Thermal decomposition of magnesium peroxotitanate to MgTiO_3

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Abstract

The DTA and DSC curves of $\text{Mg}_2[\text{Ti}_2(\text{O}_2)_4(\text{OH})_4]\cdot 4\text{H}_2\text{O}$ were recorded and used to determine 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 MgTiO_3 . The optimum conditions were also determined for obtaining MgTiO_3 with well-defined crystallinity.

Keywords: Magnesium peroxotitanate; MgTiO_3 ; DTA; DSC

1. Introduction

The synthesis and identification of a new magnesium peroxotitanate, which yields MgTiO_3 upon thermal decomposition, have been reported [1]. The aim of the study was to obtain information about the mechanism of its thermal decomposition and to determine the optimum conditions for obtaining crystalline MgTiO_3 — a compound used in the electrical industry as a dielectric.

2. Experimental

The DTA and TG curves of 60 mg of $\text{Mg}_2[\text{Ti}_2(\text{O}_2)_4(\text{OH})_4]\cdot 4\text{H}_2\text{O}$ were recorded on a MOM-OD-102 apparatus between 20 and 900°C at a heating rate of 10°C min⁻¹ in

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air or nitrogen. The exothermal and endothermal effects were examined, as well as the corresponding changes in the mass of the sample in the derivatogram and, on the basis of the information obtained, determinations were made of the temperature intervals within which additional isothermal investigations were carried out. Samples were heated to a constant mass at 10°C intervals and records were kept of the decrease of their masses in %. The sample selected was the one whose Δm coincided with the Δm from the TG curve for the temperature corresponding to the change in the TG curve and to its corresponding effect in the DTA. The mass of each initial sample was 2 g, while the temperatures determined were: 260, 400 and 580°C. The isothermal samples thus obtained were cooled and kept in a desiccator containing silica gel. Their compositions were determined by quantitative analysis: Mg, complexometrically [2]; the peroxy groups, permanganometrically [3]; Ti, gravimetrically [4]; water, by Fisher's method [5]; and the hydroxyl groups, by Chernev's method [6].

The IR spectra were taken on a Philips PV 9700 spectrograph in the region 4000 to 400 cm^{-1} in KBr tablets and, in the region of stretching vibrations of H_2O , as a suspension in hexachloro-1,3-butadiene.

The enthalpy changes accompanying the decomposition of the investigated compound were measured. The DSC curves were recorded on a Perkin-Elmer DSC-4 apparatus in air or nitrogen, in the temperature interval 20 to 450°C, at a heating rate of 10°C min^{-1} using 7.10 mg of sample.

On the basis of the data obtained, a mechanism has been proposed for the thermal decomposition of the initial $\text{Mg}_2[\text{Ti}_2(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$.

The final product, MgTiO_3 , was characterized by X-ray diffraction using a Zeiss TUR-M-62 apparatus with FeK_α radiation.

3. Results and discussion

TG, DTA and DTG curves are shown in Fig. 1, and the DSC curve is shown in Fig. 2. Table 1 contains values of the changes in the masses and the corresponding temperature intervals of the recorded stages in the derivatogram and DSC, while Table 2 presents data from the quantitative analysis of the samples heated at the selected isothermal temperatures. No differences were observed in the derivatograms obtained in air or in nitrogen.

DTA shows a fairly broad endothermal effect in the 25 to 300°C range with $T_{\text{max}} = 75^\circ\text{C}$, at which temperature the corresponding total decrease of the mass $\Delta m = 33.3\%$. The isothermal sample at $T = 260^\circ\text{C}$ corresponds to the product of this transition because it has $\Delta m = 32.5\%$, compared with $\Delta m_{\text{theor.}} = 33.0\%$. The data from its quantitative analysis (Table 2) correspond to a compound with composition $\text{Mg}_2[\text{Ti}_2\text{O}_4(\text{OH})_4]$. It follows that within this temperature range there is complete elimination of the water of hydration and of the peroxy groups of the initial compound, this being demonstrated also by the IR spectrum of the sample. It shows the absorption bands of the water of hydration (the stretching vibrations between 3600 and 3000 cm^{-1} . The bending vibration at 1630 cm^{-1}) and the absorption band at 870 cm^{-1} [7, 8] characteristic of the peroxy group are absent; these vibrations are clearly observed in

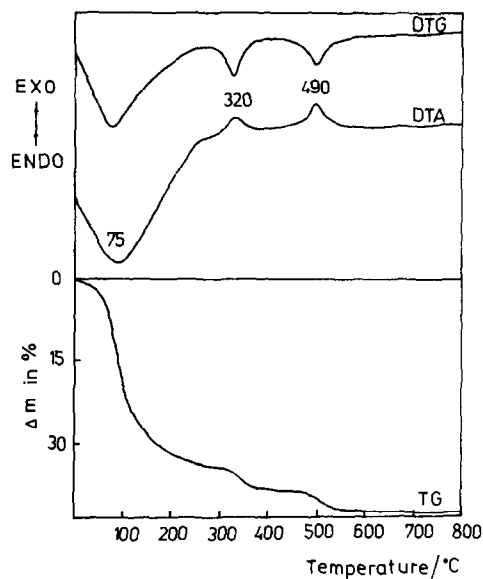


Fig. 1. DTA, DTG and TG curves of $\text{Mg}_2[\text{Ti}_2(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$.

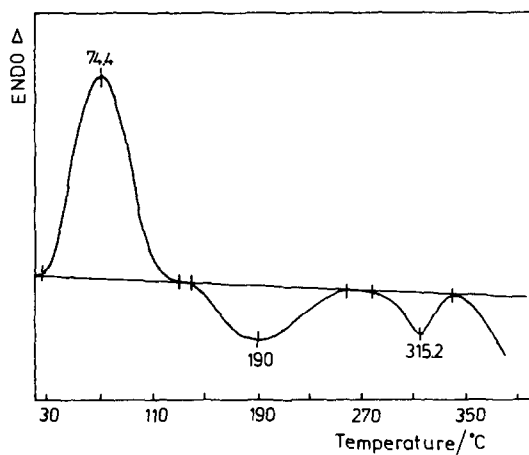


Fig. 2. DSC curves of $\text{Mg}_2[\text{Ti}_2(\text{O}_2)_4(\text{OH})_4] \cdot 4\text{H}_2\text{O}$.

the IR spectrum of the initial compound. In the examined region, the DSC curve shows an endothermic effect with $T_{\text{max}} = 74.4^\circ\text{C}$ and $\Delta H^\circ = 113 \pm 1 \text{ kJ mol}^{-1}$ and an exothermic effect with $T_{\text{max}} = 190^\circ\text{C}$ and $\Delta H^\circ = -28 \pm 0.2 \text{ kJ mol}^{-1}$ (Fig. 2). The latter is screened in DTA (Fig. 1) by the strong endothermic effect of dehydration and by separation of the peroxy groups, whereby the intermediate compound

Table 1
Data from DTA, TG and DSC curves of $\text{Mg}_2[\text{Ti}_2(\text{O}_2)_4(\text{OH})_4] \cdot 4\text{H}_2\text{O}$

Temp. interval in °C	DTA		DSC		TG	
	T_{max} in °C	T_{onset} in °C	T_{max} in °C	ΔH° in kJ mol^{-1}	Exp.	Calc.
30–300	75	32.0	74.4	113.0 ± 1	33.3	33.0
		144.1	190.0	-28.0 ± 0.2	–	–
300–400	320	301.3	315.2	-8.0 ± 0.1	37.1	37.3
400–600	490	–	–	<0	41.7	41.7

Table 2
Data from quantitative analyses of samples of $\text{Mg}_2[\text{Ti}_2(\text{O}_2)_4(\text{OH})_4] \cdot 4\text{H}_2\text{O}$ partially decomposed under isothermal conditions

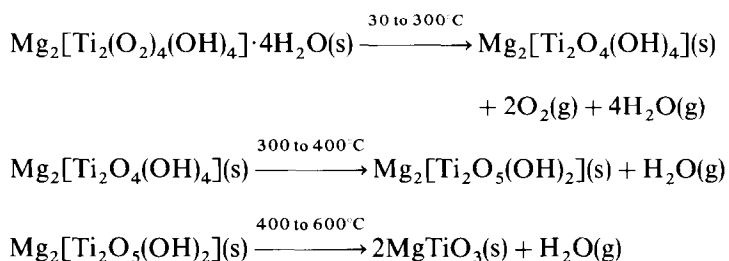
T in °C	Quantitative composition in mass%					Mol ratio in %			Δm in %	
	Mg	Ti	O_2^-	OH^-	H_2O	Mg : Ti	$:\text{O}_2^-$: OH^- : H_2O	Exp.	Calc.	
20	11.2	24.0	31.3	16.4	16.2	1.00 : 1.09 : 2.11	2.09 : 1.95	–	–	
260	16.6	35.3	–	24.2	–	1.00 : 1.09 : –	– : 2.09 : –	32.5	33.0	
400	18.5	39.1	–	12.3	–	1.00 : 1.09 : –	– : 0.95 : –	37.6	37.3	
580	19.1	40.9	–	–	–	1.00 : 1.09	– – –	41.4	41.7	

$\text{Mg}_2[\text{Ti}_2\text{O}_4(\text{OH})_4]$ is obtained. The exothermal effect could be explained by the thermodynamically greater stability of $\text{Mg}_2[\text{Ti}_2\text{O}_4(\text{OH})_4]$, compared with the initial compound. The sample obtained is amorphous to X-rays.

A slight exothermal effect is recorded in DTA with $T_{\text{max}} = 320^\circ\text{C}$. This corresponds to a decrease in the mass of the sample along the TG curve of $\Delta m = 37.1\%$. An analogous effect is observed in DSC (Fig. 2) with $T_{\text{max}} = 315.2^\circ\text{C}$ and $\Delta H^\circ = -8.0 \pm 0.1 \text{ kJ mol}^{-1}$. Corresponding to this effect is the isothermal sample obtained at $T = 400^\circ\text{C}$, with its $\Delta m = 37.6\%$. The data from the quantitative analysis (Table 2) show that a new intermediate compound is obtained at the second transition with composition $\text{Mg}_2[\text{Ti}_2\text{O}_5(\text{OH})_2]$. This compound is obtained from $\text{Mg}_2[\text{Ti}_2\text{O}_4(\text{OH})_4]$ by the separation splitting of the thermal OH^- groups, as proved by the absence of the absorption band in the IR spectrum at 1070 cm^{-1} , which is ascribed to the Ti–OH groups [9]. However, the bridging OH^- groups remain unchanged, i.e. the complex persists as a binuclear one. This is indicated by the absorption band of the bridging OH^- groups at 1415 cm^{-1} [10]. The exothermal character of the effect seen in DTA with $T_{\text{max}} = 320^\circ\text{C}$, corresponding to the process described, can be explained only by compensation of the endothermal effect of separation of the OH^- groups as water, by the bigger exothermal effect of restructuring

of the newly obtained compound $\text{Mg}_2[\text{Ti}_2\text{O}_5(\text{OH})_2]$. This is borne out also by the fact that the sample is amorphous to X-rays. Consequently, the exothermic effect is not connected with a crystallization process. An analogous explanation can be offered also for the second exothermal effect in DTA with $T_{\text{max}} = 490^\circ\text{C}$, which corresponds to decomposition of $\text{Mg}_2[\text{Ti}_2\text{O}_5(\text{OH})_2]$ to MgTiO_3 . This is proved by analysis of the final product, which corresponds to MgTiO_3 and by the recorded decrease in the mass of the sample of $\Delta m = 41.7\%$, compared with $\Delta m_{\text{theor.}} = 41.7\%$. This sample is also amorphous which again rules out the possibility of the observed exothermal effect in DTA being due to crystallization. The sample obtained by heating at $T = 580^\circ\text{C}$ to constant mass at $\Delta m = 41.4\%$ also corresponds to MgTiO_3 . It is likewise amorphous.

On the basis of the information obtained from all investigations carried out, it is possible to suggest the following mechanism for the thermal decomposition of $\text{Mg}_2[\text{Ti}_2\text{O}_4(\text{OH})_4] \cdot 4\text{H}_2\text{O}$:



An additional series of experiments was carried out in order to establish the conditions for crystallization of the amorphous MgTiO_3 obtained. Five-gram samples were heated for 2, 3, 4, 5 and 6 h in air. The X-ray diffraction pattern of the product of heating at $T = 650^\circ\text{C}$ for 2 h showed that the MgTiO_3 obtained under these conditions is crystalline. Upon increasing the duration of heating, the diffraction pattern showed increased intensity of the reflections. The same effect was observed upon increasing the temperature at which the sample was heated. The temperatures used were 650, 700, 750 and 800°C . The optimum conditions for obtaining MgTiO_3 with a fair degree of crystallinity are heating in air at 650°C for 4 h, or at 700°C for 2 h.

References

- [1] V. Parvanova and M. Maneva, *Z. Chem.* (in press).
- [2] *Komplexometrische Bestimmungsmethode mit Titriplex*, E. Merck AG, Darmstadt, 1972, p. 41.
- [3] B. Zagorchev, *Analyt. Chim.*, Technika, Sofia, 1972, p. 564.
- [4] G. Charlot, *Methods of Analytical Chemistry, Quantitative Analysis of Inorganic Compounds*, Himia, Moscow, 1965, p. 827 (in Russian).
- [5] D. Mitchell and D. Smith, *Aquametry*, Himia, Moscow, 1980, p. 35 (in Russian).
- [6] B. Chernov, *Collection of Natural Soil Activity*, ANSSSR, Moscow, 1947, p. 41 (in Russian).
- [7] W. Griffith, *J. Chem. Soc.*, 12 (1964) 5248.
- [8] G. Jere and C. Peter, *Can. J. Chem.*, 40 (1962) 1556.
- [9] K. Nakamoto, *IR Spectra of Inorganic and Coordination Compounds*, 2nd edn., Moscow, 1969, p. 89.
- [10] R. Barabanchikova, T. Limaz and M. Machossov, *Collection of Inorganic Peroxide Compounds*, Nauka, Moscow, 1975, p. 130.