

SYNTHESIS AND THERMAL DECOMPOSITION OF POTASSIUM PEROXOTITANATE TO $K_2Ti_2O_5$

V. Parvanova*

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

Potassium peroxotitanate was synthesized by the peroxy method. During the thermal decomposition $K_2Ti_2O_5$ can be obtained. The isothermal conditions for decomposition of $K_2[Ti_2(O_2)_2(OH)_6] \cdot 3H_2O$ were determined on the base of DTA, TG and DSC results. DTA and TG curves were recorded in the temperature range 20 and 900°C at a heating rate of 10°C min⁻¹. The obtained intermediate compounds were characterized by means of quantitative analysis and IR spectroscopy. The mechanism of thermal decomposition of $K_2[Ti_2(O_2)_2(OH)_6] \cdot 3H_2O$ to $K_2Ti_2O_5$ was studied. The optimal conditions for obtaining $K_2Ti_2O_5$ were determined (770°C for 10 h).

Keywords: DTA, $K_2Ti_2O_5$, potassium peroxotitanate

Introduction

In recent years, quite intensive work has been done on obtaining titanates [1–6]. They deserve special attention due to their valuable properties.

Potassium titanates having a general formula of $K_2O \cdot nTiO_2$ where $n=1–8$, depending on its composition and structure, may find application as semiconductors, photocatalyst and catalyst supports [7–9], sensors [10], ionic conductors [11]. $K_2Ti_4O_9$ is known to be applicable as inorganic ion exchanger [12] and layered host framework to synthesize inorganic–organic nanocomposite materials [13, 14]. $K_{0.5}Bi_{0.5}TiO_3$ and $K_{0.5}Bi_{0.5}TiO_3 \cdot PbZrO_3$ with ferroelectric properties were obtained by solid state reactions [15, 16].

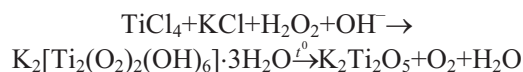
According to some literature sources [17] $K_2Ti_2O_5$, $K_4Ti_3O_8$ and $KTiO_2(OH)$ were obtained by hydrothermal oxidation of titanium metal powder with concentrated KOH solution. $K_2Ti_2O_5$ single crystals, $K_2Ti_4O_9$ whiskers and $K_2Ti_6O_{13}$ whiskers were synthesized from the TiO_2 (anatase)- K_2CO_3 starting materials by the heating calcination [18]. Fine titanate nanowires of $K_2Ti_8O_{17}$ structure with a diameter of 5–10 nm were synthesized hydrothermally via a reaction of titania particles and KOH solution [19]. $K_2Ti_4O_9$ was prepared by a solid-state reaction using nanometer-sized TiO_2 as a reactant [9].

The aim of this work is to synthesize potassium peroxotitanate by the peroxy method by the thermal decomposition of which $K_2Ti_2O_5$ to be obtained. Studying the composition of the potassium peroxotitanate, the mechanism of its thermal decomposition to $K_2Ti_2O_5$, as well as determining the optimum condi-

tions for its obtaining are of considerable scientific and practical interest. The peroxy method was selected for the synthesis of $K_2Ti_2O_5$ because no data on such studies were found in literature. This method has a number of advantages described in the previous work [20].

Experimental

By thermal decomposition of the potassium peroxotitanate $K_2Ti_2O_5$ is obtained. The potassium peroxotitanate was obtained by the peroxy method. The essence of this method may be illustrated by the following reaction:



A 20% KCl solution is added to a 30% acid solution of $TiCl_4$ in HCl. Then a 30% H_2O_2 solution is slowly added and after that a 12% NH_3 solution to pH=7. The temperature during the reaction should not exceed 5°C because the reaction is strongly exothermal. The mol ratio of the source components is $TiCl_4:KCl:H_2O_2=1:2:10$. The reaction is effected with a great excess of H_2O_2 because a considerable part of it is decomposed during the reaction. An amorphous yellow sediment of potassium peroxotitanate with a composition of $K_2[Ti_2(O_2)_2(OH)_6] \cdot 3H_2O$ is obtained. The latter is washed away till Cl^- ions are removed and then dried at a temperature not higher than 20°C in an inert environment (over 30°C starts slowly to decompose).

* vparvanova@hotmail.com

The composition of potassium peroxotitanate and the composition of the intermediate compounds obtained following the thermal decomposition were proved using the quantitative analysis and the IR spectroscopy. The Ti^{4+} and K^+ were determined spectroscopically with an ICP-AES-spectrometer Vista MPX CCD Simultaneous of the manufacturer Varian. The peroxy groups were determined permanganometrically and the hydroxyl groups – titrimetrically [21] and the water, by Fischer's method. The IR spectra were taken on a Zeiss IR-70 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.

Besides the methods described above, simultaneous DTA and TG analysis were used during the study of the mechanism of potassium peroxotitanate thermal decomposition. DTA and TG curves were recorded on MOM-OD-102 apparatus between 20 and 900°C at a heating rate of $10^\circ\text{C min}^{-1}$ in air, and the mass of the sample is 50 mg. Based on the DTA results the temperatures ($T=120, 460$ and 600°C) at which an isothermal heating of samples with a mass of 1 g were determined. The enthalpy changes were measured by DSC on a Perkin-Elmer DSC-4 apparatus, in the temperature range 20 to 400°C , at a heating rate of $10^\circ\text{C min}^{-1}$. The study was carried out in an air and nitrogen environment, and the mass of the sample is 5.2 mg.

The final product, $\text{K}_2\text{Ti}_2\text{O}_5$, was characterized by X-ray diffraction using a Zeiss TUR-M-62 apparatus with CuK_α radiation.

Results and discussion

The IR spectrum of potassium peroxotitanate at 20°C is shown on Fig. 1 and the results of the quantitative analysis of the potassium peroxotitanate and the intermediate compounds obtained via isothermal heating are shown in Table 1.

The absorption band observed at 870 cm^{-1} relates to a bidentate bonding of the peroxy group to Ti [22, 23] (Fig. 1). The bending vibration of the OH^- -groups at 1270, 1380 and 1140 cm^{-1} are of great interest. The first two bands are associated with the

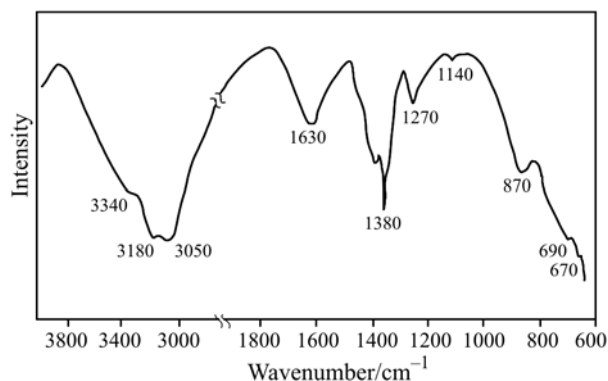


Fig. 1 IR spectra of $\text{K}_2[\text{Ti}_2(\text{O}_2)_2(\text{OH})_6]\cdot 3\text{H}_2\text{O}$

bridging OH^- -groups, and the last one to the terminal groups [24, 25]. The bending vibration of the hydrate water OH^- -group [25] at 1630 cm^{-1} is also observed in the IR spectrum. At 3340, 3180 and 3050 cm^{-1} stretching vibrations of the OH^- -groups are registered. They are impossible to be accurately identified because of the lack of structural data on the types of hydrogen bonds in which these groups participate.

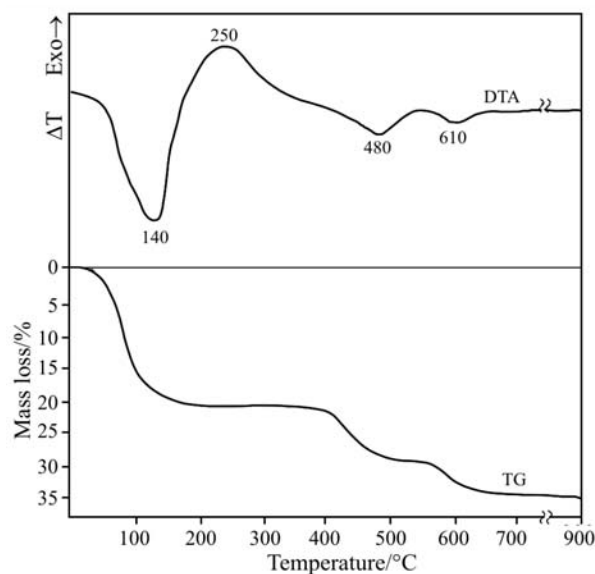
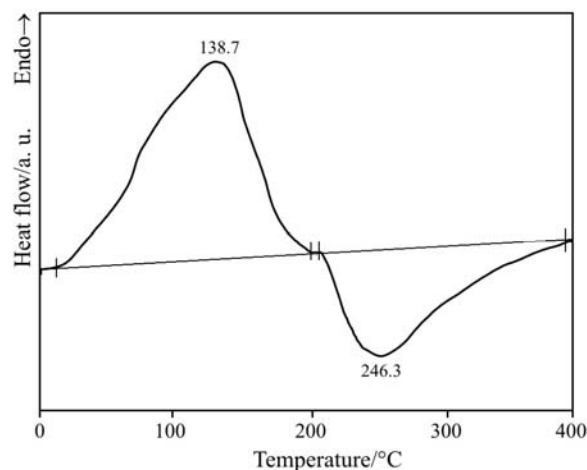
Based on the result of the quantitative analysis (at 20°C , Table 1) and of the IR spectrum (Fig. 1) one can prove that the potassium peroxotitanate has the following composition: $\text{K}_2[\text{Ti}_2(\text{O}_2)_2(\text{OH})_6]\cdot 3\text{H}_2\text{O}$.

DTA, TG and DSC curves of $\text{K}_2[\text{Ti}_2(\text{O}_2)_2(\text{OH})_6]\cdot 3\text{H}_2\text{O}$ are shown on Figs 2 and 3. The DTA and DSC data are presented in Table 2. The IR spectrum of $\text{K}_2[\text{Ti}_2(\text{O}_2)_2(\text{OH})_6]\cdot 3\text{H}_2\text{O}$ at 20°C and of the intermediate compounds obtained via isothermal heating are illustrated on Fig. 4.

A big endothermal effect with $T_{\text{max}}=140^\circ\text{C}$ is observed in the temperature range of 40 to 220°C (Fig. 2). It is associated with the simultaneous and complete separation of the hydrate water and the oxygen as a result of the decomposition of peroxy groups. A reduction of the mass $\Delta m=22.3\%$ at $\Delta m_{\text{theor}}=21.8\%$ (Table 2) was observed on this peak in the course of the TG curve (Fig. 2). The data of the IR spectrum of the sample isothermally sintered at 120°C comes in confirmation of the statement above. The absorption bands of the triangle peroxy groups at 870 cm^{-1} and of $\delta_{\text{H}_2\text{O}}$ at 1630 cm^{-1} are absent in the IR spectrum of this sample (Fig. 4b). The change of mass of this sample is

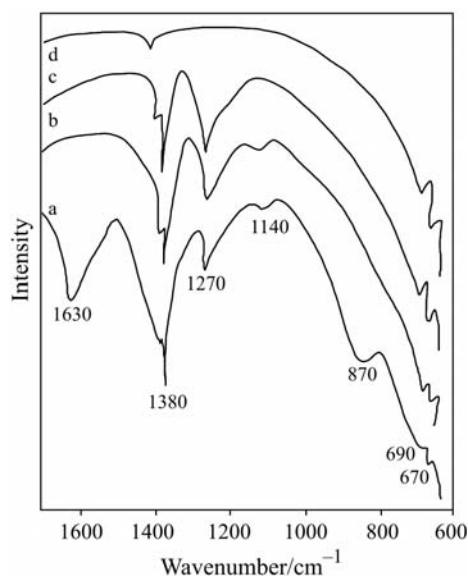
Table 1 Data from quantitative analyses of samples of $\text{K}_2[\text{Ti}_2(\text{O}_2)_2(\text{OH})_6]\cdot 3\text{H}_2\text{O}$ partially decomposed under isothermal conditions

$T/^\circ\text{C}$	Quantitative composition/mass%										Mol ratio	$\Delta m/\%$	
	calculated					experimental							
	K^+	Ti^{4+}	O_2^{2-}	OH^-	H_2O	K^+	Ti^{4+}	O_2^{2-}	OH^-	H_2O			
20	19.8	24.3	16.2	25.9	13.7	19.0	24.5	16.5	24.7	12.8	$1.00:1.05:1.06:2.99:1.46$	–	–
120	25.3	31.1	–	33.1	–	24.3	30.7	–	32.2	–	$1.00:1.03:–:3.05:–$	22.6	21.8
460	29.7	35.2	–	12.5	–	28.6	36.9	–	13.2	–	$1.00:1.05:–:1.06:–$	30.3	30.9
600	30.8	37.7	–	–	–	30.1	38.3	–	–	–	$1.00:1.04:–:–:–$	34.6	35.5


Fig. 2 DTA and TG curves of $K_2[Ti_2(O_2)_2(OH)_6] \cdot 3H_2O$

Fig. 3 DSC curve of $K_2[Ti_2(O_2)_2(OH)_6] \cdot 3H_2O$

$\Delta m_{\text{exp}}=22.6\%$ (Table 1) and it corresponds to the composition of $K_2[Ti_2O_2(OH)_6]$. An endothermic effect with $T_{\text{max}}=138.7^\circ\text{C}$ and $\Delta H^0=119\pm 1 \text{ kJ mol}^{-1}$ (Table 2) was registered in the DSC curve (Fig. 3). In spite of the better resolution of the DSC method no separation of the two effects is observed which is another confirmation that both processes are simultaneous.

The endothermic effect is immediately transformed into exothermic with $T_{\text{max}}=250^\circ\text{C}$ (Fig. 2). No


Fig. 4 IR spectra of a – $K_2[Ti_2(O_2)_2(OH)_6] \cdot 3H_2O$ at 20°C , b – heated sample at 120°C , c – heated sample at 460°C and d – heated sample at 600°C

change of mass corresponds to this effect in the TG curve, and therefore it could be assumed that this effect is probably caused by structural changes. The exothermal character of this peak is also proved by the DSC curve (Fig. 3). It has $T_{\text{max}}=246.3^\circ\text{C}$. The enthalpy of this phase transition is $\Delta H^0=-34\pm 0.5 \text{ kJ mol}^{-1}$ (Table 2).

The second weak endothermic effect has $T_{\text{max}}=480^\circ\text{C}$ (Fig. 2) and corresponds to the separation of constitutionally bound water obtained as a result of decomposition of terminal OH^- -groups. To this effect in the TG curve corresponds a change of mass $\Delta m=31.2\%$ at $\Delta m_{\text{theor}}=30.9\%$ (Table 2). The absorption band of the OH^- -groups at 1140 cm^{-1} is absent in the IR spectrum of this sample isothermally sintered at 460°C (Fig. 4c). The results of the quantitative analysis of the same sample (Table 1) confirm the decomposition of OH^- -groups, and $\Delta m_{\text{exp}}=30.3\%$. To this sample corresponds a composition of $K_2[Ti_2O_4(OH)_2]$.

The third endothermic effect has $T_{\text{max}}=610^\circ\text{C}$ (Fig. 2) and is also quite weak. To this effect in the TG curve corresponds a change of mass $\Delta m=34.8\%$ at $\Delta m_{\text{theor}}=35.5\%$ (Table 2). The effect is associated with the split of the bridging OH^- -groups. This is also proved by the IR spectrum of the sample isothermally sintered at 600°C . The absorption bands at 1270 and 1380 cm^{-1}

Table 2 Data from DTA, TG and DSC curves of $K_2[Ti_2(O_2)_2(OH)_6] \cdot 3H_2O$

Temperature range/ $^\circ\text{C}$	DTA		DSC		TG $\Delta m/\%$	
	$T_{\text{max}}/^\circ\text{C}$	$T_{\text{onset}}/^\circ\text{C}$	$T_{\text{max}}/^\circ\text{C}$	$\Delta H^0/\text{kJ mol}^{-1}$	exp.	calc.
40–220	140	77	138.7	119 ± 1.0	22.3	21.8
220–400	250	211	246.3	-34 ± 0.5	–	–
400–550	480	–	–	0>	31.2	30.9
550–660	610	–	–	0>	34.8	35.5

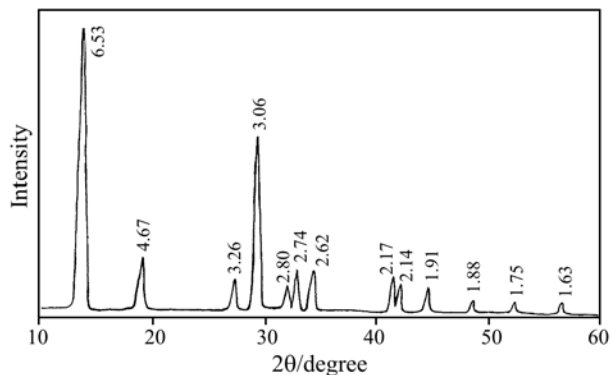
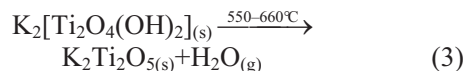
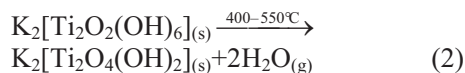
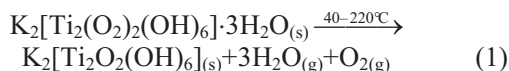


Fig. 5 XRD patterns of $K_2Ti_2O_5$ obtained at $770^\circ C$ for 10 h

corresponding to δ_{OH^-} from the Ti–O(H)–Ti-groups are absent in it (Fig. 4d). The results of the quantitative analysis of the same sample prove a reduction of the mass $\Delta m_{exp}=34.6\%$ and a composition of $K_2Ti_2O_5$ (Table 1). The X-ray analysis of the DTA sample shows that it is amorphous.

Weak peak of exothermal effects are observed in the DTA curves of peroxotitanates of the alkaline earth metals, Pb and Cd, particularly in the high-temperature area. They correspond to structural changes. Such patterns are not observed with the potassium peroxotitanate. Probably the exothermal effects are too weak and are not registered. Another possibility is that they coincide with the endothermal effects in the temperature ranges $400\text{--}660^\circ C$ and that is the reason for the weakness of the last two endothermal effects.

Based on the results of DTA, TG, DSC, the IR spectra and the quantitative analysis it is possible to suggest a probable mechanism of thermal decomposition of $K_2[Ti_2(O_2)_2(OH)_6]\cdot 3H_2O$ to $K_2Ti_2O_5$:



The optimal conditions for obtaining crystalline $K_2Ti_2O_5$ were determined. For this purpose some samples were sintered at $T=620, 680, 720, 770$ and $820^\circ C$ for 4, 6, 8, 10 and 12 h. The crystallinity of samples was determined by an X-ray analysis (Fig. 5). The samples sintered at $T=770$ and $820^\circ C$ for 10 and 12 h have diffraction lines of $K_2Ti_2O_5$ [26] and equal intensity. The optimal conditions for obtaining $K_2Ti_2O_5$ with good crystallinity are $770^\circ C$ for 10 h.

Conclusions

Potassium peroxotitanate was synthesized by the peroxo method by the thermal decomposition of which $K_2Ti_2O_5$ can be obtained. The chemical compositions of the potassium peroxotitanate and of the intermediate compounds obtained as a result of the thermal decomposition were determined.

Based on the results of DTA, TG, DSC, the IR spectra and the quantitative analysis a mechanism of thermal decomposition of $K_2[Ti_2(O_2)_2(OH)_6]\cdot 3H_2O$ to $K_2Ti_2O_5$ was suggested.

The optimal conditions for obtaining $K_2Ti_2O_5$ were determined ($770^\circ C$ for 10 h).

References

- 1 S. Grujić, N. Blagojević, M. Tošić, V. Živanović and B. Božović, *J. Therm. Anal. Cal.*, 83 (2006) 463.
- 2 S. Aoyagi, Y. Kuroiwa, A. Sawada, H. Kawaji and T. Atake, *J. Therm. Anal. Cal.*, 81 (2005) 627.
- 3 M. Donaldson, R. Stevens, B. E. Lang, J. Boerio-Goates, B. F. Woodfield, R. L. Putnam and A. Navrotsky, *J. Therm. Anal. Cal.*, 81 (2005) 617.
- 4 G. C. Lin, X. M. Xiong, J. X. Zhang and Q. Wei, *J. Therm. Anal. Cal.*, 81 (2005) 41.
- 5 M. A. F. de Souza, A. G. Souza, R. A. Candea, D. M. A. Melo, L. E. B. Soledade, M. R. C. Santos, I. M. G. Santos, S. J. G. Lima and E. Longo, *J. Therm. Anal. Cal.*, 79 (2005) 411.
- 6 M. R. S. Silva, S. C. Souza, I. M. G. Santos, M. R. Cassia-Santos, L. E. B. Soledade, A. G. Souza, S. J. G. Lima and E. Longo, *J. Therm. Anal. Cal.*, 79 (2005) 421.
- 7 M. Machida, X. W. Ma, H. Taniguchi, J. Yabunaka and T. Kijima, *J. Mol. Catal. A: Chem.*, 155 (2000) 131.
- 8 M. Yanagisawa, S. Ucida, S. Yin and T. Sato, *Chem. Mater.*, 13 (2001) 174.
- 9 J. Yang, *J. Mater. Sci.*, 40 (2005) 3765.
- 10 A. M. Katayama, H. Hasegawa, T. Noda, T. Akiba and H. Yanagida, *Sens. Actuators B*, 2 (1992) 143.
- 11 S. Kikkawa, F. Yasuda and M. Koizumi, *Mater. Res. Bull.*, 20 (1985) 1221.
- 12 T. Sasaki, M. Watanabe, Y. Komatsu and Y. Fujiki, *Inorg. Chem.*, 24 (1985) 2265.
- 13 M. Ogawa and Y. Takizawa, *Mol. Cryst. Liq. Cryst. Sci. Technol. A*, 341 (2000) 357.
- 14 M. He, X. Feng, X.-H. Lu, X.-Y. Ji, C. Liu, N.-Z. Bao and J.-W. Xie, *J. Mater. Sci.*, 39 (2004) 3745.
- 15 T. Zaremba, *J. Therm. Anal. Cal.*, 74 (2003) 653.
- 16 T. Zaremba, *J. Thermal Anal.*, 54 (1998) 63.
- 17 N. Masaki, S. Uchida, H. Yamane and T. Sato, *J. Mater. Sci.*, 35 (2000) 3307.
- 18 N.-Z. Bao, X. Feng, X.-H. Lu and Z.-H. Yang, *J. Mater. Sci.*, 37 (2002) 3035.

- 19 Z. Y. Yuan, X. B. Zhang and B. L. Su, *Appl. Phys. A*, 78 (2004) 1066.
- 20 V. Parvanova, *J. Therm. Anal. Cal.*, 84 (2006) 589.
- 21 E. V. Shamrikova, T. A. Sokolova and I. V. Zaboeva, *Eurasian Soil Sci.*, 38 (2005) 471.
- 22 G. Jere and C. Pater, *Can. J. Chem.*, 40 (1962) 1556.
- 23 W. Griffith, *J. Chem. Soc.*, 12 (1964) 5248.
- 24 R. Barabanchikova, T. Limar and M. Mochossov, *Collection of Inorganic Peroxide Compounds*, Nauka, Moscow 1975, p. 130 (in Russian).
- 25 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley and Sons, New York 1978, p. 230.
- 26 JCPDS-51-1890.

Received: April 18, 2006

Accepted: June 16, 2006

DOI: 10.1007/s10973-006-7669-0