

## THERMAL DECOMPOSITION OF CUPRUM PEROXOTITANATE TO $\text{CuTi}_2\text{O}_5$

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### ABSTRACT

The DTA, TG and DSC curves of  $\text{Cu}[\text{Ti}_2(\text{O}_2)_2(\text{OH})_6] \cdot 2\text{H}_2\text{O}$  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  $\text{CuTi}_2\text{O}_5$ . The optimum conditions were also determined for obtaining  $\text{CuTi}_2\text{O}_5$  with well-defined crystallinity.

**Keywords:** cuprum peroxotitanate,  $\text{CuTi}_2\text{O}_5$ , DTA.

### INTRODUCTION

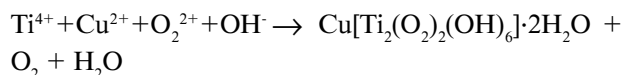
In the last years it has been working on the creation of microwave materials on the base of multi-component compositions containing  $\text{Cu}^{2+}$ . In a set of references it is cited that in a certain quantitative range of  $\text{Cu}^{2+}$  increases the ceramic density and leads to improving of the quality factor [1]. Ceramics containing  $\text{Cu}^{2+}$  can be used for multilayered microwave devices obtained by a low-temperature presintering method [2]. In their case the temperature of calcinations is reduced from 1200 to 1000°P without reduction of the permittivity ( $\epsilon_r$ ) [3]. The measurements of the resonators confirm the potential use of such materials for small planar antennas. These materials are attractive for capacitor applications and certainly for microelectronics, and microwave devices (cell mobile phones), where the miniaturization of the devices is crucial [4, 5].

The aim of the present investigation is to obtain  $\text{CuTi}_2\text{O}_5$  by a thermal decomposition of Cu-peroxotitanates.  $\text{CuTi}_2\text{O}_5$  will be used as a component in the material of a microwave resonator. The Cu-

peroxotitanate is synthesized by peroxomethod [6]. Its composition is proved by the methods of the quantitative analysis and IR-spectroscopy. A scheme for thermal decomposition of Cu-peroxotitanates to  $\text{CuTi}_2\text{O}_5$  is suggested on the base of the data from DTA, TG and XRD analysis. The optimum conditions for obtaining of fine crystalline  $\text{CuTi}_2\text{O}_5$  are determined.

### EXPERIMENTAL

The Cu-peroxotitanate was synthesized by a peroxomethod [7, 8].  $\text{TiCl}_4$  acid solution was added to 20%  $\text{CuSO}_4$  solution, 30%  $\text{H}_2\text{O}_2$  solution and 12%  $\text{NH}_3$  solution to  $\text{pH} = 7.5$ . The process can be described with the following scheme:



Amorphous Cu-peroxotitanate sediment is obtained. The Cu-peroxotitanate is isothermally calcinated at  $T = 730^\circ\text{C}$  for 2 hours or at  $T = 680^\circ\text{C}$  for 3.5 hours whereat  $\text{CuTi}_2\text{O}_5$  is obtained.

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The composition of the intermediate compounds and of  $\text{CuTi}_2\text{O}_5$  was proved by the methods for quantitative analysis and IR-spectra. The peroxo groups were determined permanganometrically [9]; the hydroxyl groups - by Chernev's method [10], water - by Fisher's method [11].  $\text{Cu}^{2+}$  and  $\text{Ti}^{4+}$  were determined by ICP-AES-spectrometer. The IR spectra were taken on a Philips PV 9700 spectrometer in the region 4000 to 400  $\text{cm}^{-1}$  in KBr tablets and in the region of stretching vibrations of  $\text{H}_2\text{O}$ , as a suspension in hexachloro-1,3-butadiene.

The thermal decomposition of Cu-peroxotitanate is studied by DTA and DSC methods. The derivatograph investigations were recorded on a MOM-OD-102 instrument in the temperature range of 20-900°C in air at heating rate of 10°C  $\text{min}^{-1}$  and a mass sample of 40 mg. The DSC curves were recorded on a Perkin Elmer DSC-4 instrument from 20 to 400°C, at a heating rate of 10°C and a mass sample of 5.8 mg.

The final product,  $\text{CuTi}_2\text{O}_5$ , was characterized by X-ray diffraction using a Zeiss TUR-M-62 instrument with  $\text{CuK}_\alpha$  radiation.

## RESULTS AND DISCUSSION

The results of the quantitative analysis of Cu-peroxotitanate and the intermediate compounds are shown in Table 1 and their IR-spectra on Fig. 1 and Fig. 2. The X-ray analysis of the Cu-peroxotitanate at 20°C shows an amorphous phase and has the following composition:  $\text{Cu}[\text{Ti}_2(\text{O}_2)_2(\text{OH})_6]\cdot 2\text{H}_2\text{O}$  (Table 1). The typical absorption bands of the structural groups forming the compound can be observed in its IR-spectrum (Figs. 1 and 2a). The absorption band at 870  $\text{cm}^{-1}$  corresponds to the peroxo group which is bonded to the titanium forming a triangle [12, 13]. The wide absorption band with maximum values at 580  $\text{cm}^{-1}$  is due to the stretching vibration of the Ti-O bond [14]. The absorption bands at 1050, 1120 and 1360  $\text{cm}^{-1}$  are of interest in the observed spectrum. The first two are typical of the bending vibration of the terminal Ti-OH groups [15], and the third one - of the bridging Ti-O(H)-Ti

Table 1. Data from quantitative analyses of samples of Cu-peroxotitanate and intermediate compounds.

T, °C	Quantitative composition/mass %					Mol ratio					$\Delta m/\%$	
	$\text{Cu}^{2+}$	$\text{Ti}^{4+}$	$\text{O}_2^{2-}$	OH	$\text{H}_2\text{O}$	$\text{Cu}^{2+} : \text{Ti}^{4+} : \text{O}_2^{2-} : \text{OH} : \text{H}_2\text{O}$	$\Delta m_{\text{exp.}}$	$\Delta m_{\text{calc}}$				
20	17.9	26.6	18.3	28.4	9.8	1.00 : 1.97 : 2.03 : 5.92 : 1.93	-	-				
150	21.3	32.9	-	34.2	-	1.00 : 2.05 : - : 6.06 : -	18.8	19.4				
400	25.2	36.3	-	13.0	-	1.00 : 1.92 : - : 1.93 : -	10.5	10.2				
670	26.9	39.4	-	-	-	1.00 : 1.94 : - : - : -	5.5	5.1				

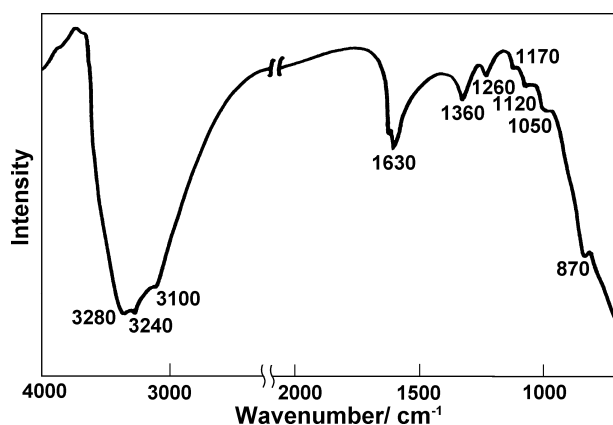


Fig. 1. IR spectra of  $\text{Cu}[\text{Ti}_2(\text{O}_2)_2(\text{OH})_6]\cdot 2\text{H}_2\text{O}$ .

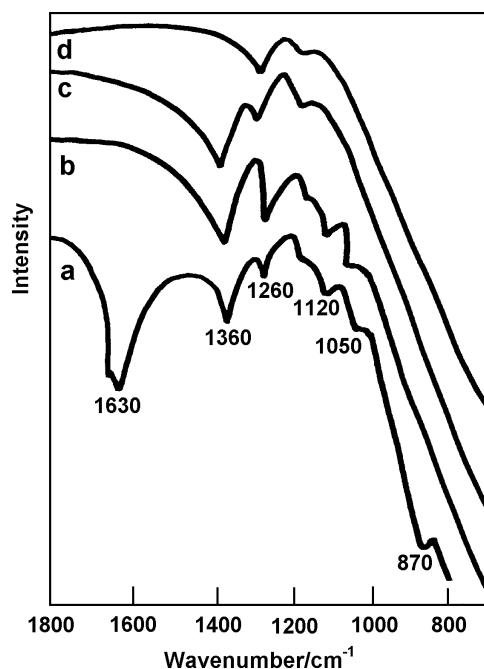


Fig. 2. IR spectra of: a)  $\text{Cu}[\text{Ti}_2(\text{O}_2)_2(\text{OH})_6]\cdot 2\text{H}_2\text{O}$  at  $T=20^\circ\text{C}$ ; b) heated sample at  $T=150^\circ\text{C}$ ; c) heated sample at  $T=400^\circ\text{C}$ ; d) heated sample at  $T=670^\circ\text{C}$ .

groups [16]. The existence of bridging OH<sup>-</sup> groups is a proof for the presence of binuclear structure of the complex ion. The observed absorption bands of the stretching vibration of OH<sup>-</sup> in H<sub>2</sub>O at 3280 cm<sup>-1</sup> and  $\delta_{H_2O}$  at 1630 cm<sup>-1</sup> point to the presence of hydrate water.

DTA, TG and DSC-curves of Cu-peroxotitanate are shown on Figs. 3 and 4. The DTA, TG and DSC results are presented in Table 2. As seen on Fig. 3, the first strong and large endothermic effect covers the temperature range 30-275°C and has  $T_{max} = 171^\circ\text{C}$ . It is explained with the simultaneous and full separation of the hydrate water and the peroxy groups. This is a result both from the reduction of the mass of sample  $\Delta m_{exp.} = 18.8\%$  at  $\Delta m_{calc.} = 18.4\%$  observed along the TG-curve (Fig. 3, Table 2), and from the IR-spectra (Fig. 2b). The absorption bands of the triangle peroxy group at 870 cm<sup>-1</sup> and of the hydrate water at 1630 cm<sup>-1</sup> disappear in the spectrum of the sample calcinated at  $T = 150^\circ\text{P}$ . This fact is further confirmed by the results of the isothermally calcinated sample at 150°P (Table 1). The mass of the sample is changed to  $\Delta m_{exp.} = 19.0\%$  and corresponds to the composition  $\text{Cu}[\text{Ti}_2\text{O}_2(\text{OH})_6]$ . The enthalpy of the first phase transition, as determined by DSC (Fig. 4), is  $\Delta H^\circ = 171.6 \pm 1.0 \text{ kJ mol}^{-1}$  and the effect is maximum at  $T = 167.2^\circ\text{C}$ .

The second strong endothermic effect with  $T_{max} = 430^\circ\text{C}$  is due to the separation of two H<sub>2</sub>O molecules from the terminal Ti-OH groups. It is characterized in the TG-curve with change of mass  $\Delta m_{exp.} = 9.8\%$  at  $\Delta m_{calc.} = 10.2\%$  (Fig. 3, Table 2). This is confirmed by the IR-spectrum of the sample calcinated at  $T = 400^\circ\text{C}$ . It lacks the absorption bands at 1050 and 1120 cm<sup>-1</sup> corresponding to the bending vibration of the terminal Ti-OH groups (Fig. 2c). Table 1 shows that change of mass of the isothermally calcinated sample  $\Delta m_{exp.} = 10.5\%$  can be observed at this temperature as well as reduction of the hydroxyl groups from 6.06 to 1.93 mol. The composition of this sample is  $\text{Cu}[\text{Ti}_2\text{O}_4(\text{OH})_2]$ .

Table 2. Data from DTA, TG and DSC-curves of  $\text{Cu}[\text{Ti}_2(\text{O}_2)_2(\text{OH})_6] \cdot 2\text{H}_2\text{O}$ .

DTA		DSC			TG $\Delta m/\%$	
Temp.interval/ $^\circ\text{C}$	$T_{max}/^\circ\text{C}$	$T_{onset}/^\circ\text{C}$	$T_{max}/^\circ\text{C}$	$\Delta H^\circ/\text{kJmol}^{-1}$	Exp.	Calcd.
30-290	171	107	167.2	$171.6 \pm 1.0$	19.0	19.4
295-370	335	283	325.7	$-56.1 \pm 0.2$	-	-
380-525	430	-	-	0>	9.8	10.2
525-600	584	-	-	<0	-	-
625-720	700	-	-	0>	5.4	5.1
720-800	740	-	-	<0	-	-

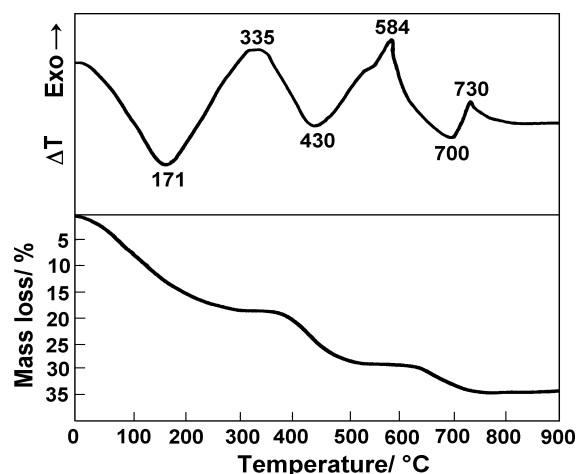


Fig. 3. DTA, and TG curves of  $\text{Cu}[\text{Ti}_2(\text{O}_2)_2(\text{OH})_6] \cdot 2\text{H}_2\text{O}$ .

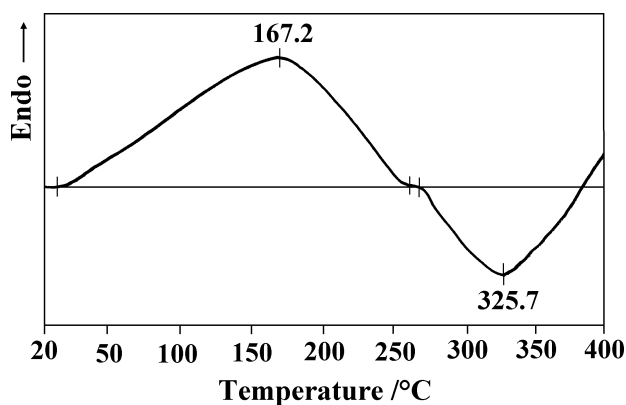


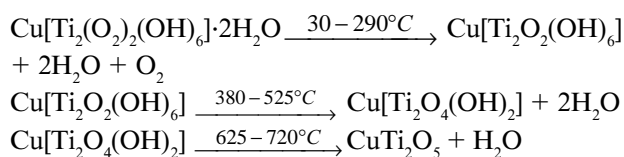
Fig. 4. DSC curve of  $\text{Cu}[\text{Ti}_2(\text{O}_2)_2(\text{OH})_6] \cdot 2\text{H}_2\text{O}$ .

The third weak endothermic effect within the temperature range 625-720°C with  $T_{max} = 700^\circ\text{C}$  is associated with the separation of the last water molecule most likely from the bridging OH<sup>-</sup> groups. It is characterized in the TG-curve with change of mass  $\Delta m_{exp.} = 5.4\%$  at  $\Delta m_{calc.} = 5.1\%$  (Fig. 3, Table 2). The phase transition corresponding to the bridging OH<sup>-</sup> groups decomposition can be very well explained with the IR-spectrum of the isothermally calcinated sample at 670°C. The absorption band of the Ti-O(H)-Ti groups at 1360 cm<sup>-1</sup> can be also observed (Fig. 2d). Another evidence in support of the statement above is the result of the quantitative analysis of a sample calcinated at 670°C (Table 1). It is characterized with change of mass  $\Delta m_{exp.} = 35.5\%$  at  $\Delta m_{calc.} = 34.7\%$  and a composition  $\text{CuTi}_2\text{O}_5$ .

The progress of the DTA-curve points to the presence of three exo-

thermal effects: the first one at  $T_{\max} = 335^{\circ}\text{C}$ , the second one at  $T_{\max} = 585^{\circ}\text{C}$  and the third one at  $T_{\max} = 730^{\circ}\text{C}$ . They are not characterized with change of mass in the TG-curve. Therefore, all three exothermal effects correspond to phase transformations of the substance in more thermodynamically stable phases. The enthalpy of the first exothermal effect at  $T = 325.7^{\circ}\text{C}$ , as determined by DSC (Fig. 4) is  $\Delta H^{\circ} = 56.1 \pm 0.2 \text{ kJ mol}^{-1}$ .

Based on the DTA, TG, IR-spectrum and the quantitative analysis results, here is the most probable diagram of thermal decomposition of  $\text{Cu}[\text{Ti}_2(\text{O}_2)_2(\text{OH})_6] \cdot 2\text{H}_2\text{O}$  to  $\text{CuTi}_2\text{O}_5$ :



The X-ray analysis of the  $\text{CuTi}_2\text{O}_5$  obtained from DTA at  $T=730^{\circ}\text{C}$  shows an amorphous phase. No other exothermal effect is observed to the end of the DTA-curve ( $900^{\circ}\text{C}$ ) which allows the presupposition that  $\text{CuTi}_2\text{O}_5$  does not crystallize at the speed of making the derivatogram ( $10^{\circ}\text{C min}^{-1}$ ). However, samples of the initial Cu-peroxotitanate isothermally calcinated at  $T = 730^{\circ}\text{C}$  for 2 hours and at  $T = 680^{\circ}\text{C}$  for 3.5 hours decomposed to fine-crystalline  $\text{CuTi}_2\text{O}_5$ .

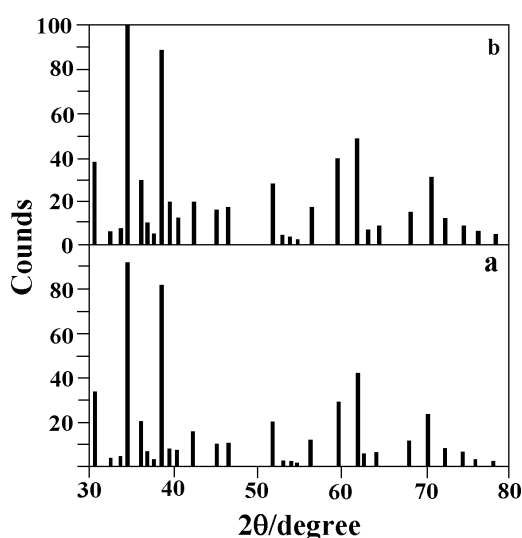


Fig. 5. Schematic diagram of the X-ray diffraction lines for  $\text{CuTi}_2\text{O}_5$  obtained at: a)  $730^{\circ}\text{C}$  for 2h; b)  $680^{\circ}\text{C}$  for 5h.

## CONCLUSIONS

Cu-peroxotitanate was synthesized by a peroxo-method and after thermal decomposition  $\text{CuTi}_2\text{O}_5$  was obtained.

Based on the DTA, TG, IR-spectrum and the quantitative analysis results, here is the most probable diagram of thermal decomposition of  $\text{Cu}[\text{Ti}_2(\text{O}_2)_2(\text{OH})_6] \cdot 2\text{H}_2\text{O}$  to  $\text{CuTi}_2\text{O}_5$ .

The optimal conditions for obtaining fine-crystalline  $\text{CuTi}_2\text{O}_5$  were determined for the electronic industry. The calcination of  $\text{Cu}[\text{Ti}_2(\text{O}_2)_2(\text{OH})_6] \cdot 2\text{H}_2\text{O}$  in an aerial atmosphere at  $T = 730^{\circ}\text{C}$  for 2 hours and at  $T = 680^{\circ}\text{C}$  for 3.5 hours.

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