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THERMAL DECOMPOSITION OF LEAD PEROXOTITANATE TO $PbTiO_3$

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The DTA and DSC curves of $Pb_2[Ti_2(O_2)_2(O)_2(OH)_4]\cdot H_2O$ 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 $PbTiO_3$. The optimum conditions were also determined for obtaining $PbTiO_3$ with well-defined crystallinity.

Keywords: *DSC, DTA, lead peroxotitanate, PbTiO$_3$*

Introduction

Titanates have valuable properties that defines the interest in obtaining of these compounds [1–6]. The mixed $PbTiO_3$ ceramics show good and interesting characteristics. High Curie temperature (T_c), low relative dielectric constant (ε_r), large anisotropy of the electromechanical coupling factors (K) and high pyroelectric coefficient (P) make them suitable for designing of: ultrasonic diagnosis transducers, underwater transducers, high frequency SAW filters and pyroelectric infrared sensors [7–9].

$PbTiO_3$ is obtained by decomposition of $Pb_2[Ti_2(O_2)_2(O)_2(OH)_4]\cdot H_2O$. Lead peroxotitanate possesses some important advantages compared to the conventional precursors ($PbCO_3$ and TiO_2). When it is used the lead titanate's synthesis temperature is considerably lower, T=450°C, the reaction time is shorter 1–2 h. The milling and homogenizing of $Pb_2[Ti_2(O_2)_2(O)_2(OH)_4]\cdot H_2O$ is avoided. The obtained $PbTiO_3$ possesses higher purity, fine crystal structure (less than 1 μm) and homogeneous grain size composition.

The object of the present investigation is to obtain information about the mechanism of thermal decomposition of $Pb_2[Ti_2(O_2)_2(O)_2(OH)_4]\cdot H_2O$ to $PbTiO_3$ by the help of DTA, DSC, X-ray analysis, IR-spectrum and quantitative analysis. Then, the optimum parameters for the preparation of $PbTiO_3$ are determined.

Experimental

The lead peroxotitanate is obtained by the peroxomethod [10, 11] and its synthesis can be expressed with the following scheme:

$$TiCl_4+PbCl_2+H_2O_2+OH^- \rightarrow$$

$$Pb_2[Ti_2(O_2)_2(O)_2(OH)_4]\cdot H_2O$$

15% solution of $PbCl_2$ and 30% H_2O_2 is added to $TiCl_4$. 12% NH_3 is also added to obtain pH=8.5. The temperature of the reaction is 14–15°C. What is obtained is an amorphous sediment of peroxocompound. It is calcinated in air and obtained $PbTiO_3$.

The DTA and TG curves of 45 mg of $Pb_2[Ti_2(O_2)_2(O)_2(OH)_4]\cdot H_2O$ were recorded on MOM-OD-102 apparatus between 20 and 900°C at a heating rate of 10°C min^{-1} in air or nitrogen. The endothermal effects, 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 samples 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 1 g, while the temperatures determined were: 140, 250 and 500°C. The isothermal samples thus obtained were cooled and kept in a desiccator containing silica gel. Their compositions were determined by quantitative analysis: Pb, complexometrically [12]; the peroxo groups, permanganometrically [13]; Ti, gravimetrically [14]; water, by Fisher's method [15]; and the hydroxyl groups, by Chernev's method [16].

The IR spectra were taken on a Philips PV 9700 spectograph in the region 4000 to 400 cm^{-1} in KBr

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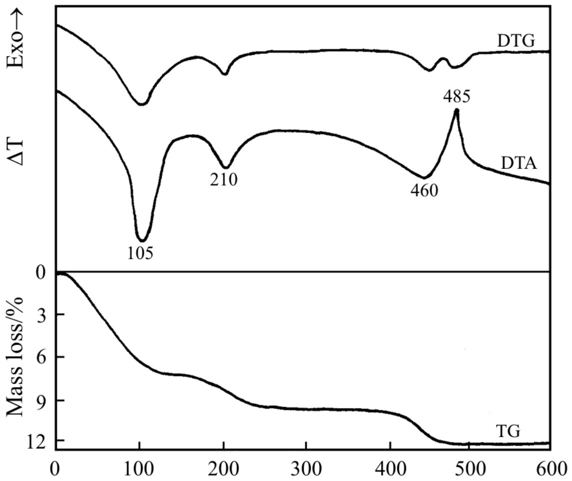

Fig. 1 DTA, DTG and TG curves of $Pb_2[Ti_2(O_2)_2(O)_2(OH)_4]\cdot H_2O$

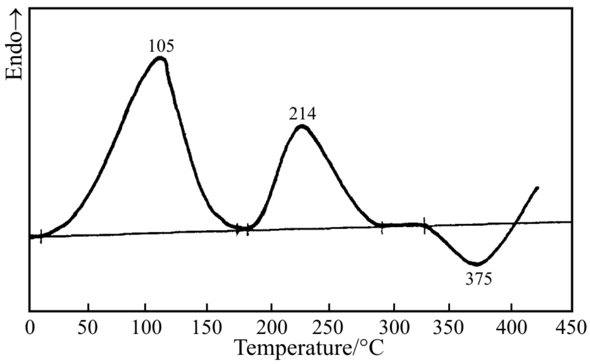

Fig. 2 DSC curve of $Pb_2[Ti_2(O_2)_2(O)_2(OH)_4]\cdot H_2O$

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 5.15 mg of sample.

The final product, $PbTiO_3$, was characterized by X-ray diffraction using a Zeiss TUR-M-62 apparatus with CuK_α radiation.

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 sample heated at the selected isothermal temperatures. No difference were observed in the derivatograms obtained in the air or in nitrogen. In Fig. 3 the IR spectrum of $Pb2[Ti_2(O_2)_2(O)_2(OH)_4]\cdot H_2O$ in the range from 4000 to 400 cm^{-1} and Fig. 4a the spectrum of the same compound but in the range from 2000 to 400 cm^{-1} are shown.

DTA shows an endothermal effect in the 30 and 160°C range with T_{max}=105°C, at which temperature on the TG-curve corresponds total decrease of the mass Δm=7.5%. The isothermal sample at T=140°C corresponds to the product of this transition because it has Δm=7.1%, compared with $\Delta m_{theor.}$=7.2%. The data from its quantitative analysis (Table 2) corresponds to a compound with composition $Pb_2[Ti_2(O)_4(OH)_4]$. It follows that within this temperature range there is complete elimination of the water of hydration and of the peroxo groups of the initial compound, this being demonstrated

Table 1 Data from DTA, TG and DSC curves of $Pb_2[Ti_2(O_2)_2(O)_2(OH)_4]\cdot H_2O$

DTA		DSC			TG Δm/%	
Temp. interval/°C	T_{max}/°C	T_{onset}/°C	T_{max}/°C	ΔH^0/kJ mol^{-1}	exp.	calcd.
30–160	105	72.0	105	96±1.0	7.5	7.2
160–250	210	201.3	214	38±0.5	9.6	9.8
–	–	346.5	375	–10±0.1	–	–
250–475	460	–	–	0>	12.3	12.4
475–500	485	–	–	<0	–	–

Table 2 Data from quantitative analyses of samples of $Pb_2[Ti_2(O_2)_2(O)_2(OH)_4]\cdot H_2O$ partially decomposed under isothermal conditions

T/°C	Quantitative compositon/mass%					Mol ratio	Δm/%	
	Pb^{2+}	Ti^{4+}	O_2^{2-}	OH^-	H_2O	$Pb:Ti:O_2^{2-}:OH^-:H_2O$	exp.	calcd.
20	59.7	14.1	9.2	9.9	2.6	1.00:1.02:1.00:2.02:0.50	–	–
140	64.0	15.5	–	10.5	–	1.00:1.05:–:2.00:–	7.1	7.2
250	65.3	15.4	–	5.5	–	1.00:1.02:–:1.03:–	9.9	9.8
500	67.9	16.9	–	–	–	1.00:1.03:–:–:–	12.6	12.4

also by the IR spectrum of the sample (Fig. 4b). It shows the absorption bands of the water of hydration (the stretching vibrations between 3500 and 3000 cm^{-1}, the banding vibration at 1635 cm^{-1}) and the absorption band at 840 cm^{-1} [17, 18] characteristic of the peroxo group are absent; these vibrations are clearly observed in the IR spectrum of the initial compound (Fig. 3). In the examined region, the DSC curve shows an endothermal effect with T_{max}=105°C and ΔH^0=96±1.0 kJ mol^{-1} (Fig. 2). The latter is screened in DTA (Fig. 1) by the strong endothermal effect of dehydration and by separation of the peroxo groups, whereby the intermediate compound $Pb_2[Ti_2(O)_4(OH)_4]$ is obtained. This sample is amorphous to X-rays.

A small endothermal effect is recorded in DTA with T_{max}=210°C. This corresponds to the decrease of the mass of the sample along the TG curve of Δm=9.6%. An analogous effect is observed in DSC (Fig. 2) with T_{max}=214°C and ΔH^0=38±0.5 kJ mol^{-1}. Corresponding to this effect is the isothermal sample obtained at T=250°C, with its Δm=9.9%. The data from the quantitative analysis (Table 2) show that a new intermediate compound is obtained at the second transition with composition $Pb_2[Ti_2(O)_5(OH)_2]$. This compound is obtained from $Pb_2[Ti_2(O)_4(OH)_4]$ by the separation splitting of the terminal OH$^-$ groups, as proved by the absence of the absorption band in the IR spectrum (Fig. 4c) at 1073 cm^{-1}, which is ascribed to the Ti–OH groups [19]. However, the bridging OH$^-$ groups remain in changed, i.e. the complex persist as a binuclear one. This is indicated by the absorption band of the bridging OH$^-$ groups at 1285 cm^{-1} [20].

The exothermal character of the effect is observed in DSC curve (Fig. 2) with T_{max}=375°C and ΔH^0=–10 kJ mol^{-1}. Because of the weak effect, it is not registered in the DTA-curve. At this temperature in the TG curve a change of the sample mass is not observed. This effect can be explained only by the restructuring of the newly obtained compound $Pb_2[Ti_2(O)_5(OH)_2]$. This is borne out by the fact that the sample is amorphous to X-rays. Consequently, the exothermal effect is not connected with a crystallization process.

The third endothermal effect on the DTA curve with T_{max}=460°C (Fig. 1) is immediately transformed into an exothermal effect. To this effect shown in the TG-curve correspond decrease of the mass Δm=12.3% at $\Delta m_{theor.}$=12.4%. The mentioned effect is in accordance to the separation of the bridging OH$^-$ groups as water from $Pb_2[Ti_2(O)_5(OH)_2]$. This is proved by the IR-spectrum. Absorption band of bridging OH$^-$ groups at 1285 cm^{-1} absence (Fig. 4d). The sample obtained by heating at T=500°C to constant mass has Δm=12.6%. It is X-rays crystalline and corresponds to $PbTiO_3$ diffraction lines.

The exothermal effect in the DTA curve at T_{max}=485°C can be explained by the structure changes connected with the formation of thermodynamically stable $PbTiO_3$. Changes of the mass do not correspond this effect in the TG curve. The sample is amorphous to X-rays. Consequently, the exothermal effect is not connected with a crystallization process.

No other effect is to be observed in the DTA curve until the end and this justifies the assumption that, at the heating rate applied (10°C min^{-1}) the obtained $PbTiO_3$ does not crystallize. However, the sample of the starting lead peroxotitanate heated

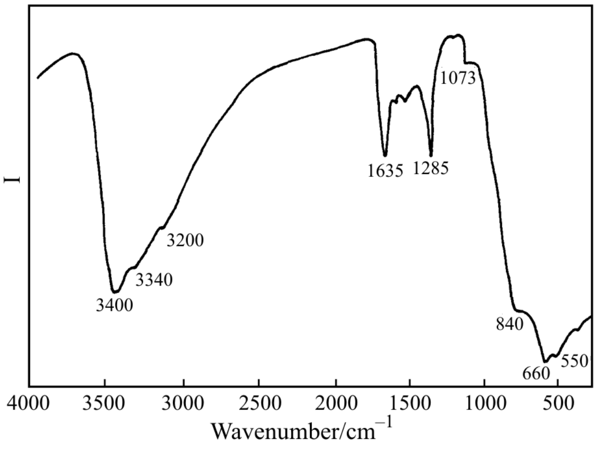

Fig. 3 IR spectrum of $Pb_2[Ti_2(O_2)_2(O)_2(OH)_4]\cdot H_2O$

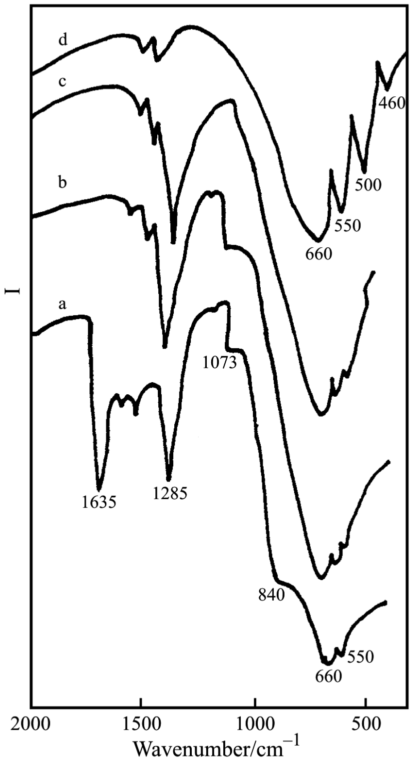

Fig. 4 IR spectra of: a – initial sample at T=20°C; b – heated sample at T=140°C; c – heated sample at T=250°C; and d – heated sample at T=500°C

isothermally at *T*=485°C for 2 h shows the diffraction patterns of crystalline $PbTiO_3$ [21].

On the basis of the information obtained from investigations carried out, it is possible to suggest the following mechanism for the thermal decomposition of $Pb_2[Ti_2(O_2)_2(O)_2(OH)_4]\cdot H_2O$:

$$Pb_2[Ti_2(O_2)_2(O)_2(OH)_4]\cdot H_2O_{(s)} \xrightarrow{30-300°C}$$

$$Pb_2[Ti_2(O)_4(OH)_4]_{(s)}+H_2O_{(g)}+O_{2(g)}$$

$$Pb_2[Ti_2(O)_4(OH)_4]_{(s)} \xrightarrow{160-250°C}$$

$$Pb_2[Ti_2(O)_5(OH)_2]_{(s)}+H_2O_{(g)}$$

$$Pb_2[Ti_2(O)_5(OH)_2]_{(s)} \xrightarrow{250-500°C}$$

$$2PbTiO_{3(s)}+H_2O_{(g)}$$

An additional series of experiments was carried out in order to establish the conditions for crystallization of the amorphous $PbTiO_3$ obtained. Five-gram samples were heated for 1, 2, 3, 4 and 5 h in air. The X-ray diffraction pattern of the product of heating at *T*=450°C for 2 h showed that the $PbTiO_3$ obtained under these conditions is crystalline. Upon increasing the duration of heating, the diffraction patterns showed increased intensity of the reflections. The same effect was observed upon increasing the temperature at which the sample was heated. The temperature used were 450, 500, 550 and 600°C. The optimum conditions for obtaining $PbTiO_3$ with a fair degree of crystallinity are heating in air at 450°C for 2 h, or at 550°C for 1 h (Fig. 5).

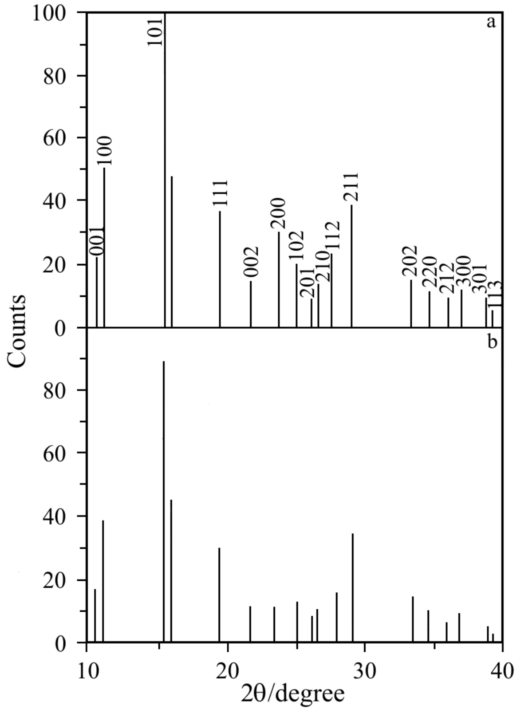

Fig. 5 Schematic diagram of the X-ray diffraction lines for $PbTiO_3$ obtained at: a – 450°C for 2 h; b – 550°C for 1 h

Conclusions

On the basis of the date of DTA, DSC, IR-spectroscopy, quantitative and X-ray analysis, a mechanism has been proposed for the thermal decomposition of $Pb_2[Ti_2(O_2)_2(O)_2(OH)_4]\cdot H_2O$ to $PbTiO_3$.

The optimum conditions for obtaining $PbTiO_3$ with a fair degree of crystallinity are heating of $Pb_2[Ti_2(O_2)_2(O)_2(OH)_4]\cdot H_2O$ in air at 450°C for 2 h, or at 500°C for 1 h.

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