

SYNTHESIS AND THERMAL DECOMPOSITION OF BARIUM PEROXYTITANATE TO BARIUM TITANATE

L. Genov, M. Maneva and V. Parvanova

HIGHER INSTITUTE OF CHEMICAL TECHNOLOGY, 1156 SOFIA, BULGARIA

Barium peroxytitanate, $\text{Ba}_2[\text{Ti}_2(\text{O}_2)_4(\text{OH})_4(\text{H}_2\text{O})_4]$, was synthesized and its thermal decomposition in the temperature range from 298 to 1173 K was investigated. The intermediates at 423, 533, 773 and 873 K were identified by means of quantitative analysis, IR spectroscopy and X-ray diffraction analysis. On the basis of the data obtained, a scheme of its thermal decomposition was suggested.

Isothermal treatment was carried out at 873 and 973 K for different periods. The optimum conditions of preparation of tetragonal barium titanate with high crystallinity were determined, i.e. annealing for 390 min at 873 K.

The available data on the synthesis and the structure of barium peroxytitanate are quite scanty and inexact. Barabanshikova et al. have synthesized peroxytitanates of alkaline earth elements [1] by adding $\text{Ti}(\text{OH})_4$ and a solution of $\text{M}(\text{NO}_3)_2$, where $M = \text{Ca}, \text{Sr}$ or Ba , to a solution of NH_3 and H_2O_2 at 293–298 K. Formation of a binuclear complex has been suggested. The structure of the latter, however, is somewhat nuclear in view of the electroneutrality of the molecule. In a patent [2], some data were given about the conditions of preparation of barium peroxytitanate from a soluble titanate salt, without discussion of the problem of its molecular structure. Only the problem of its thermal decomposition to barium titanate was considered.

The object of the present investigation was to synthesize barium peroxytitanate with a definite composition and to suggest the probable scheme of its thermal decomposition to BaTiO_3 through identification of the intermediates. Then, on the basis of the information obtained, the optimum parameters for the preparation of a tetragonal, well-crystallized barium titanate could be determined.

The methods of quantitative analysis, IR spectroscopy and X-ray diffraction phase analysis were used in these investigations.

Experimental

Barium peroxytitanate with composition $\text{Ba}_2[\text{Ti}_2(\text{O}_2)_4(\text{OH})_4(\text{H}_2\text{O})_4]$ was prepared in the following way: to a solution of TiCl_4 and BaCl_2 in a mole ratio of 1:1 was added an 8-fold excess (relative to the mole ratio) of 30% H_2O_2 , and the solution was neutralized with 10% ammonia solution to pH 9–9.5. During the experiment, the temperature was kept at 283 ± 2 K. The pale-yellow residue obtained was filtered, rinsed and dried to constant weight.

The TG–DTG–DTA diagrams of the barium peroxytitanate were recorded with a MOM derivatograph at a heating rate of 10 deg min^{-1} up to 1173 K.

The DSC curve was recorded with a Perkin–Elmer DSC at a heating rate of 10 deg min^{-1} in the temperature range 370–540 K.

The intermediates of the thermal decomposition were obtained by heating the initial compound at 423, 533, 773, 873 or 933 ± 2 K for 30 min (to constant weight), after heating at a rate of 10 deg min^{-1} to the respective temperatures. They were identified by quantitative analysis and IR spectroscopy. Barium and titanium were determined gravimetrically [3, 4], the peroxy groups by titration with permanganate [5], the hydroxy groups by the method of Chernov [6], and water by the Fischer method.

The IR spectra were recorded in the range from 3800 to 1800 cm^{-1} in a suspension with Hostafion and from 1800 to 400 cm^{-1} in KBr tablets with a Zeiss spectrophotometer UR–10.

The intermediates obtained at the respective temperatures investigated were annealed for 30, 90, 150, 210, 330, 390 or 450 min, and a diffractogram of each sample was recorded with a Zeiss TUR M–62 apparatus, Cu-K_α radiation being used.

Results and discussion

The DTA and TG curves of barium peroxytitanate are shown in Fig. 1, and the DSC curves in Fig. 2. The quantitative analysis data on the intermediates are listed in Table 1, and their IR spectra, compared with the spectrum of the initial compound, are given in Fig. 3. The information from the X-ray diffraction analyses is plotted in Figs 4 and 5.

The DTA curve (Fig. 1) shows a broad endoeffect with maximum at 433 K and a weak exoeffect at $T_{\text{max}} = 883$ K. The enthalpy of the first phase transition, as determined by DSC (Fig. 2) is $175.5 \text{ kJ mol}^{-1}$ and the effect is maximum at 408 K. It is to be noted, however, that there are no other maxima in the temperature range between the two effects in the DTA and DSC curves, while in the same region the TG

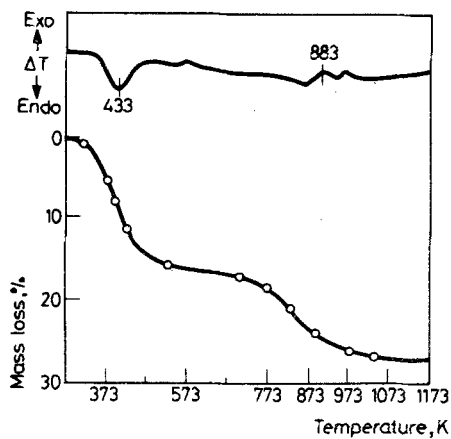
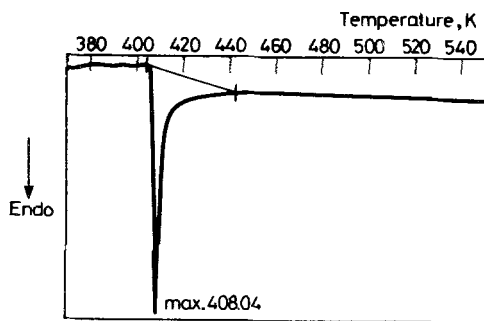

 Fig. 1 DTA and TG data at heating rate of 10 deg/min⁻¹

 Fig. 2 DSC data at a heating rate of 10 deg/min⁻¹. WT = 3.77 mg

Table 1 Quantitative analysis data on the intermediates of thermal decomposition of Ba₂[Ti₂(O₂)₄(OH)₄(H₂O)₄]

T, K	%					Ratio		Δm, %	
	Ba	Ti	O ₂ ²⁻	OH ⁻	H ₂ O	Ba:Ti:O ₂ ²⁻ :OH ⁻ :H ₂ O	found	calcd.	
285	42.59	16.37	20.4	10.1	11.5	1:1.1:2.06:2:2.09	—	—	
423	46.79	18.02	1.4	11.3	12.9	1:1.1:0.1:1.96:2.08	9.8	10.0	
533	54.08	20.11	—	13.1	1.0	1:1.1:0:2:0.14	10.8	11.3	
773	55.92	21.12	—	6.87	—	1:1.1:0:1	3.0	2.8	
873	57.95	22.10	—	—	—	1:1.1	2.6	2.8	
933	57.99	22.12	—	—	—	1:1.1	—	—	

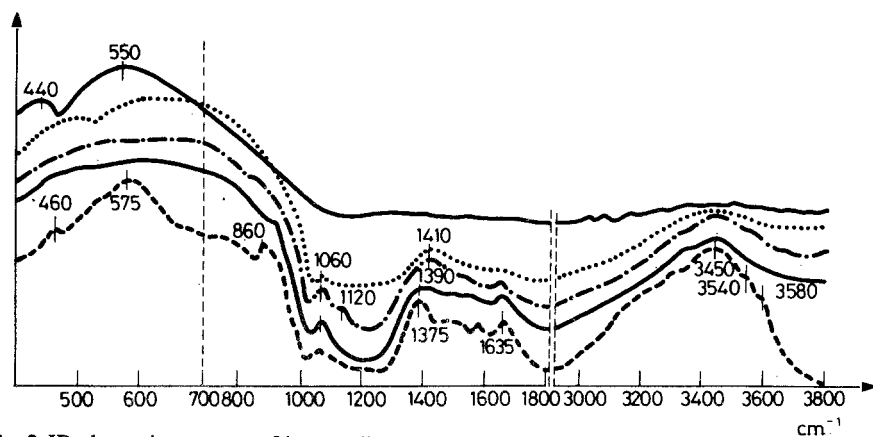
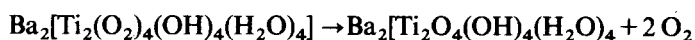


Fig. 3 IR absorption spectra of intermediate products: --- at 285 K; — at 423 K; - · - · - at 523 K; · · · at 773 K; — — — at 873 K

curve changes its direction and shows a gradual decrease in mass. In this region, therefore, phase transition occur, but the respective enthalpy changes are insignificant and are not recorded. Information about the character of the latter can be obtained from the compositions of the intermediates, from the weight changes (Table 1) and from the IR spectra (Fig. 3).

In the IR spectrum of the sample heated at 423 K (Fig. 3), there is no absorption band due to the triangular peroxy group $\text{Ti} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array}$ [7-9], as a weak vibration is observed at that position. This fact is confirmed by the data in Table 1, which show that the quantity of peroxide decreases quickly from 20.4 to 1.2%. The binuclear complex remains, however, as seen from the characteristic absorption of the bridging OH groups at 1375 cm^{-1} , also observed in the spectrum of the initial barium peroxytitanate. In the region of the vibrations of the coordinated water at 575 cm^{-1} [10], a broad plateau is observed. However, the presence of a bending vibration of the water molecule at 1635 cm^{-1} , and also the broad absorption band of the stretching vibrations ν_{OH} , confirm the existence of hydrate water in the intermediates identified. The vibrations of the OH groups [10] overlap with the stretching vibrations of the water in the respective region [10], and the quantity of OH groups increases slightly according to Table 1. Thus, the information from the IR spectra, together with the quantitative analysis data on the contents of Ba, Ti and H_2O , as well as the mass loss recorded in the TG curve, $\Delta m = 9.8\%$ ($\Delta m_{\text{calcd.}} = 10.0\%$), permit the assumption that the endoeffect at 433 K is due to the transition:



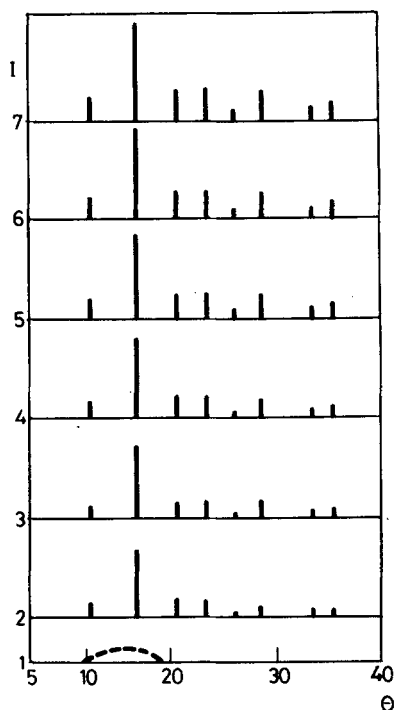
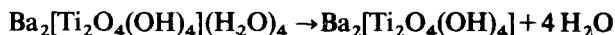


Fig. 4 X-ray diffraction diagram of the products heated at 873 K for 1 – 30 min; 2 – 90 min; 3 – 150 min; 4 – 210 min; 5 – 330 min; 6 – 390 min; 7 – 450 min

Analysis of the spectrum of the intermediate at 533 K proves the presence of bridging OH groups, the Ti–OH bond and a small quantity of water. These data, correlated with the quantitative analysis data on Ba, Ti, O_2^- , OH^- and H_2O (Table 1) and the mass loss, can be explained in terms of removal of the hydrate water. The absence of an endoeffect associated with the suggested transition shows that the removal of water, which is dehydrated earlier at 433 K, starts slowly and gradually at slightly higher temperatures. This suggestion is verified by the higher value of the enthalpy corresponding to the only observed endoeffect in the DTA curves. With regard to these considerations, the transition can be defined as:



The intermediate at 773 K has a spectrum which is quite similar to that at 533 K. The contents of Ba and Ti in it are still in a ratio of 1:1.1, and the content of OH Groups is reduced. The absence of an endoeffect in the DTA curve, and the mass loss recorded by TG, can be explained by the formation of an unstable intermediate according to the scheme:

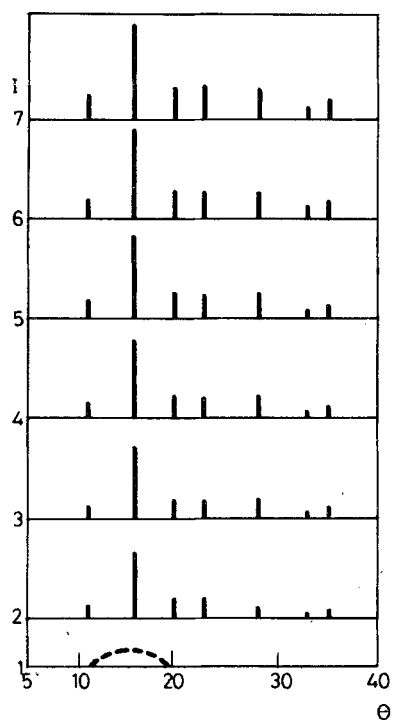
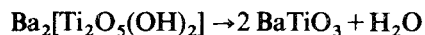


Fig. 5 X-ray diffraction diagram of the products heated at 973 K for 1 – 30 min; 2 – 90 min; 3 – 150 min; 4 – 210 min; 5 – 330 min; 6 – 390 min; 7 – 450 min



Reference [1] mentions the presence of OH groups in the product of thermal decomposition of barium peroxytitanate at 773 K. Those groups, however, are not registered at higher temperatures.

The exothermic DTA effect (Fig. 1) with maximum at 883 K corresponds to the transition of the unstable intermediate to barium titanate. The characteristic absorption bands for this product, with maxima at 550 and 440 cm^{-1} , are observed in the spectrum. The phase transition is also identified via the recorded weight change of the sample, and it can be represented as:



BaTiO_3 obtained under the conditions of thermal decomposition is amorphous to X-rays, as confirmed by its diffractogram (Fig. 4).

A very slight exoeffect is recorded in the DTA curve at about 973 K, which is not

associated with a weight change in the TG plot. The diffractogram of this product also reveals an amorphous state, and thus we should not talk about crystallization of the initial amorphous BaTiO_3 ; this is probably due to the heating rate.

It is interesting to check whether the duration of annealing of the sample of amorphous BaTiO_3 leads to its crystallization and, if so, what kind of epigony is formed. Accordingly, the samples obtained at 873 and 973 K were annealed for a longer time, i.e. 30, 90, 150, 210, 330 or 350 min; the resulting diffractograms are shown in Figs 4 and 5. It is seen that BaTiO_3 crystallizes in a tetragonal structure after a longer annealing. The data show that, at the two temperatures investigated, annealing for 90 min is necessary to obtain the reflections characteristic of tetragonal barium titanate. The crystallinity of the product is improved up to 390 min, however, after which appreciable changes are not observed.

Thus, it was established that barium peroxytitanate had to be annealed at 873 K for 390 min for its conversion into well-crystallized tetragonal BaTiO_3 .

References

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Zusammenfassung — Bariumperoxotitanat $\text{Ba}_2[\text{Ti}_2(\text{O}_2)_4(\text{OH})_4(\text{H}_2\text{O})_4]$ wurde dargestellt und seine thermische Zersetzung im Temperaturbereich 298–1173 K untersucht. Die bei 423, 533, 773 und 873 vorliegenden Zwischenprodukte wurden durch quantitative Analyse, IR-Spektroskopie und Röntgenbeugung untersucht. Nach den Ergebnissen wurde ein Ablaufschema der thermischen Zersetzung vorgeschlagen. Isotherme Behandlung über unterschiedliche Zeiten bei 873 und 973 K ergaben als optimale Bedingungen für die Präparation von Bariumtitanat hoher Kristallinität 390 min bei 873 K.

Резюме — Синтезирован пероксититанат бария — $\text{Ba}_2[\text{Ti}_2(\text{O}_2)_4(\text{OH})_4(\text{H}_2\text{O})_4]$ — и изучено его термическое разложение в интервале температур 298–1173 К. Методом количественного анализа, ИК спектроскопии и рентгенофазового анализа идентифицированы промежуточные

продукты, образующиеся при температурах 423, 533, 773 и 873 К. На основе полученных данных предложена схема его термического разложения. Изотермическая обработка образца была проведена при температурах 873 и 973 К в различные периоды времени отжига. Оптимальными условиями получения высококристаллического титаната бария с тетрагональной структурой была температура 873 К и время отжига 390 минут.