

Formation and Use of $\text{BaO} \cdot \text{TiO}_2 \cdot x\text{H}_2\text{O}$ Hydrogel Prepared from Titanium Peroxocomplex as Precursor of the BaTiO_3 Phase

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Hydrogels $\text{BaO} \cdot \text{TiO}_2 \cdot x\text{H}_2\text{O}$ were prepared by the coprecipitation of Ba^{2+} ions and Ti(IV) peroxocomplex with solution of NH_3 . The process of precipitation was followed potentiometrically. The stoichiometric coprecipitation was achieved at $\text{pH} > 12$. The BaTiO_3 phase formation starts at the temperature $\approx 600^\circ\text{C}$.

The formation of homogeneous hydrogels or products for the preparation of pure stoichiometric ceramic products, occasionally used as chemical standards, by the sol-gel process is at present an exceedingly important procedure of material preparation. A considerable attention has been paid to the preparation by $\text{BaO} \cdot \text{TiO}_2 \cdot x\text{H}_2\text{O}$ hydrogel method [1]. The preparation of BaTiO_3 phase by sol-gel process is the enhancement of its properties from the viewpoint of achievement of the high homogeneity of the prepared material and the high surface activity of obtained material particles needed for sintering. This preparation usually starts from barium and titanium acetate complexes and continues by subsequent precipitation with NaOH (or NH_3 solution) or begins directly from organometallic barium and titanium compounds *via* their dissolution and precipitation. The final stage of the preparation of BaTiO_3 is based on hydrogel heating at temperatures $> 80^\circ\text{C}$. The BaTiO_3 has been prepared by hydrolysis of alcoholates at a lower temperature [2, 3]. Other methods of preparation comprise the coprecipitation of barium and titanium in the form of oxalates and hydrothermal precipitation at higher pressure and temperature. Moreover, the method of the BaTiO_3 preparation by the calcination of homogeneous hydrogel at the temperature over 800°C [4] can also be used.

In this study, we aimed at the possibility of $\text{BaO} \cdot \text{TiO}_2 \cdot x\text{H}_2\text{O}$ hydrogel formation by precipitating Ti(IV) and Ba^{2+} ions from the solution of titanium(IV) peroxocomplex and BaCl_2 with $\text{NH}_3(\text{aq})$ – which has not been used yet – and by the following BaTiO_3 phase preparation.

EXPERIMENTAL

3 cm^3 of H_2O_2 (30 %, anal. grade) and 0.1 cm^3 of TiCl_4 (reagent grade) were added into 40 cm^3 of distilled H_2O and the solution was thoroughly stirred. The amount of dissolved BaCl_2 (anal. grade) corre-

sponding to the stoichiometric ratio $n(\text{BaO})/n(\text{TiO}_2) = 1/1$ was added into the solution 30 min later. The precipitation was brought about with 5 % solution of NH_3 (anal. grade). An overflow microburette was used for titration with the NH_3 solution. The course of precipitation was followed by measuring pH and potentiometrically (Radelkis OP 208, Budapest, Pt indication electrode and calomel reference electrode). The formed hydrogel was filtered, washed with distilled water and dried at 105°C for 2 h. The formation of the BaTiO_3 phase at different calcination temperatures was investigated by infrared spectroscopy (Specord M80, Zeiss, Jena). The thermal effects accompanying the chemical transformations of hydrogel and the loss of mass with temperature were investigated by DTA and TG analysis (Derivatograph Q 1500 D, MOM, Budapest). The $n(\text{Ba})/n(\text{Ti})$ ratio in the precipitated product was determined using the flame AAS method (AAS 3, Zeiss, Jena) after dissolution of calcinate (prepared by treating the precipitated hydrogel at 1000°C for 1 h) in HCl (35 %, anal. grade). The VIS light absorption by the Ti(IV) peroxocomplex was measured at 400 nm (Hitachi UV 1100). The product obtained by calcination at 1000°C was analyzed by X-ray diffraction analysis (Mikrometa) using $\text{CuK}\alpha$ radiation at angles 2θ from 20° to 60° and by infrared spectroscopy (Specord M80, Zeiss, Jena). The morphology and particle size of hydrogel and calcinated product was estimated by scanning electron microscopy (SEM) (Tesla BS 340).

RESULTS AND DISCUSSION

In Fig. 1 the Pt electrode potential change for different reactants is shown as a function of the added volume of NH_3 solution. (The added volume of NH_3 solution was calculated relatively to the equivalent point of curve 1.) Curve 1 describes the titration of the titanium peroxocomplex with the NH_3 solution according to the equation

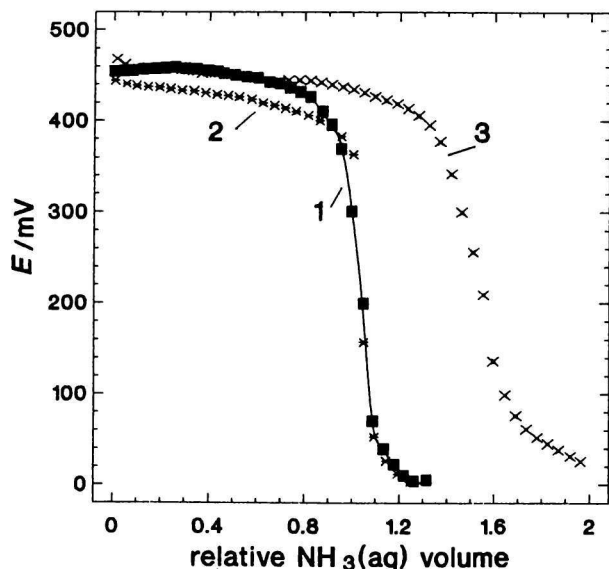


Fig. 1. The change of potential electrode as a function of relative volume of NH₃(aq) (calculated as a ratio of added NH₃(aq) volume and NH₃(aq) volume in the equivalence point of curve 1) for titration of TiCl₄ + H₂O₂ (1), H₂O₂ + HCl (2), TiCl₄ + H₂O₂ + BaCl₂ (3).

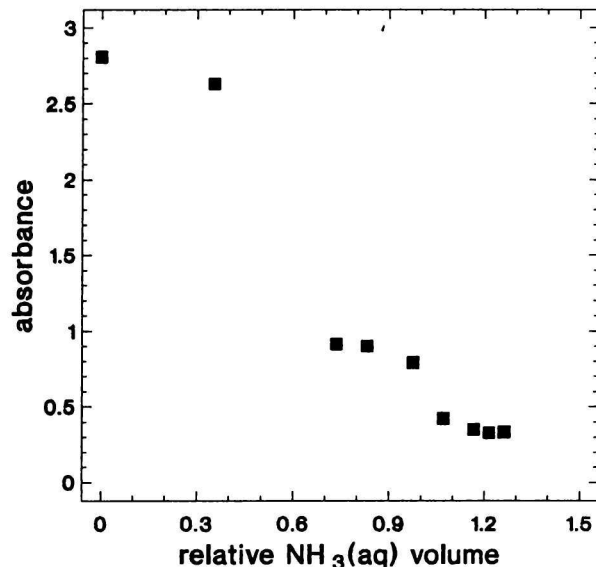
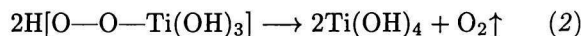


Fig. 3. The absorbance of Ti(IV) peroxocomplex vs. relative NH₃(aq) volume at the wavelength of 400 nm.

added or originating from decomposition of the titanium(IV) peroxocomplex with NH₃ solution. Analysis of these curves indicates that the equivalence points of curves 1 and 2 are identical and correspond to the sum of NH₃(aq) volumes necessary for titration of equivalent amounts of H₂O₂ and Cl⁻ ions present or arising from the decomposition of peroxocomplex yielding peroxyacid. The pH change of Ti(IV) peroxocomplex solution as a function of added NH₃ solution volume is shown in Fig. 2 (curve 1). Fig. 2 points out the significantly acidic character of the arising hydrogel. It can be seen that the added NH₃ volume corresponds to the total amount of the HCl (due to the equivalence point on potentiometric titration curve) released according to eqn (1) and is by 30 % lower than the added NH₃ volume at the point corresponding to pH ≈ 7.

This result is in agreement with Ref. [5], in which a considerably acidic character of Ti(IV) peroxyacid was shown as well as chance of decomposition of old hydrogels according to



The plot of the absorbance of Ti(IV) peroxocomplex against the volume of the added NH₃ solution at the wavelength of 400 nm is shown in Fig. 3. The lowest value of absorbance is very close to the equivalence point determined potentiometrically.

The change of the potential due to titration of the solution containing Ti(IV) peroxocomplex and BaCl₂ (ratio $n(\text{Ba}) : n(\text{Ti}) = 1 : 1$) with the NH₃ solution is shown in Fig. 1 (curve 3). The by 50 % higher volume of added NH₃ at the equivalence point compared with titration of the solution without presence of Ba²⁺ ions corresponds to the titration of BaCl₂ according to the

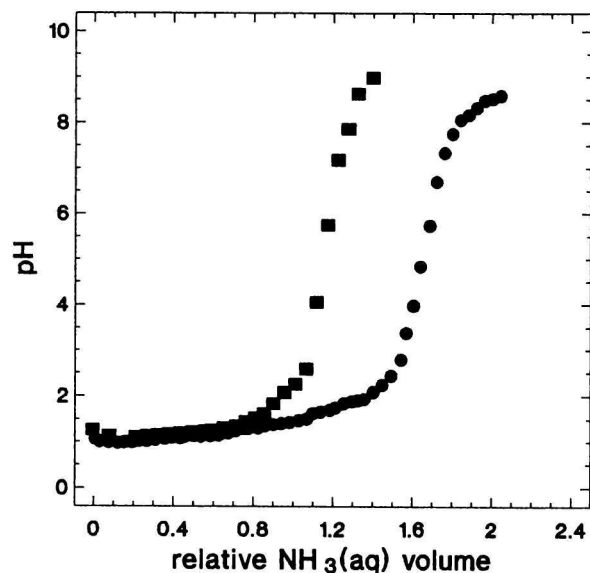
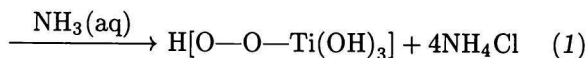
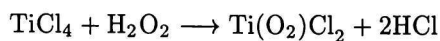
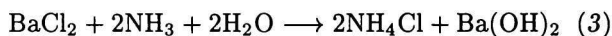


Fig. 2. The pH of solution as a function of the relative NH₃(aq) volume for titration of the solution of TiCl₄ + H₂O₂ (■) and TiCl₄ + H₂O₂ + BaCl₂ (●).



giving rise to the precipitate of peroxotitanic acid. Curve 2 corresponds to the titration of the solution containing equimolar amounts of H₂O₂ and HCl,

equation



and the final equation of coprecipitation is given by the sum of eqns (1) and (3). The simple potentiometric wave was found on curve 3, having verified the homogeneous coprecipitation of Ti(IV) and Ba^{2+} ions, without preferred precipitation of any of them. The beginning of the precipitation corresponds to about 80 % of the relative NH_3 volume under formation of big membranous precipitates, being dissolved during stirring.

Fig. 2 (curve 2) shows the change in pH during the titration with NH_3 solution. The acidity of formed hydrogel was the same as the Ti(IV) peroxyacid acidity.

The quantitative analysis of the content of Ba^{2+} and Ti(IV) in the dried hydrogel by the flame AAS method has shown that the quantitative precipitation of Ba^{2+} ions requires a high pH value ($\text{pH} > 12$) of solution; otherwise the precipitation is not quantitative (as much as 8 mass % Ba is not precipitated).

The analysis of aggregates by SEM has shown that the average size of hydrogel particles is about $0.2 \mu\text{m}$.

The results of the DTA and TG analysis of hydrogel with the ratio $n(\text{Ba}) : n(\text{Ti}) = 1$ showed that the hydrogel decomposition starts at the temperature 150°C and is terminated at 550°C . The exoeffect was observed on DTA curve simultaneously with the mass loss at the temperature of 590°C (Fig. 4). It has been found by measuring the infrared spectra of the products obtained at different temperatures (Fig. 5) that BaTiO_3 is formed at the temperature corresponding to the exoeffect registered by DTA analysis and mass loss coincides with the decrease of CO_2 specific IR absorption at the wavenumber about 1500 cm^{-1} corresponding to decomposition of BaCO_3 , created by absorption of CO_2 in the solution from air.

The X-ray diffraction spectrum of the final product, being formed by calcination of Ba—Ti hydrogel at the temperature of 1000°C , is shown in Fig. 6. The spectrum gives evidence of the presence of the BaTiO_3 phase.

The resulting BaTiO_3 particles, observed by SEM, have an angular form and their size exceeds $100 \mu\text{m}$; these properties point out a high activity of the formed hydrogel from the viewpoint of sintering.

CONCLUSION

The preparation of $\text{BaO} \cdot \text{TiO}_2 \cdot x\text{H}_2\text{O}$ hydrogel by coprecipitation of Ti(IV) and Ba^{2+} ions is characterized by a slow engagement of Ba^{2+} ions and Ti(IV) into the hydrogel without preferential precipitation of any of them. This fact is an assumption for obtaining sufficiently homogeneous hydrogel. For the stoichiometric precipitation of Ba^{2+} ions, the $\text{pH} > 12$ must be achieved. The BaTiO_3 phase already forms

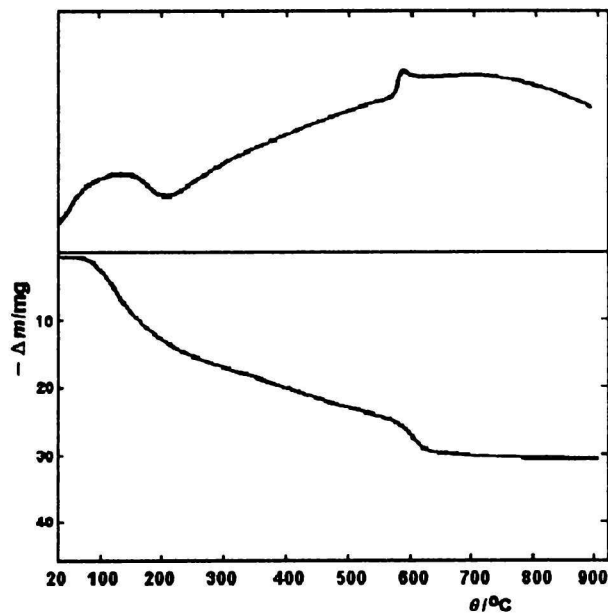


Fig. 4. DTA and TG analysis of the prepared Ba—Ti hydrogel.

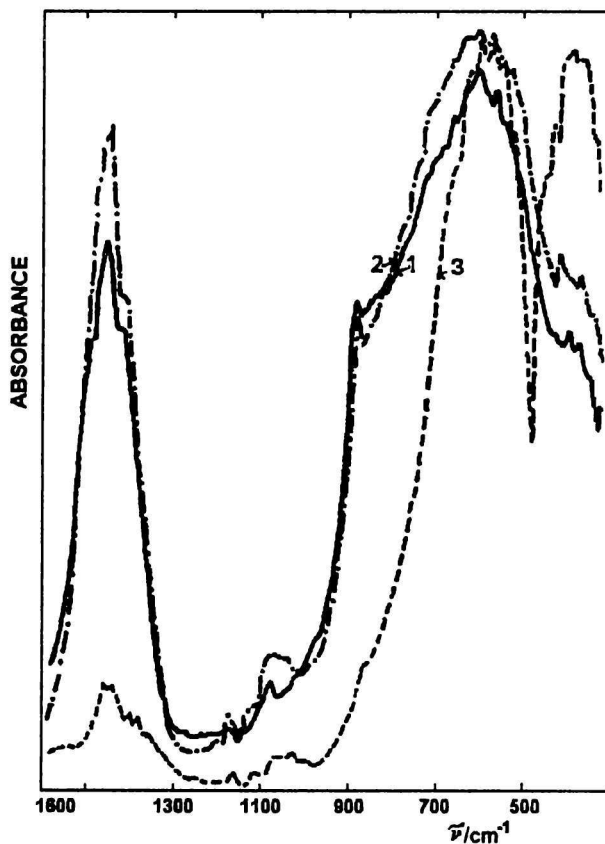


Fig. 5. The IR spectra of the calcinated Ba—Ti hydrogel obtained at different temperatures: 200°C (1), 400°C (2), 600°C (3).

at 600°C and it is advantageous from the viewpoint of using this powder product for the preparation of

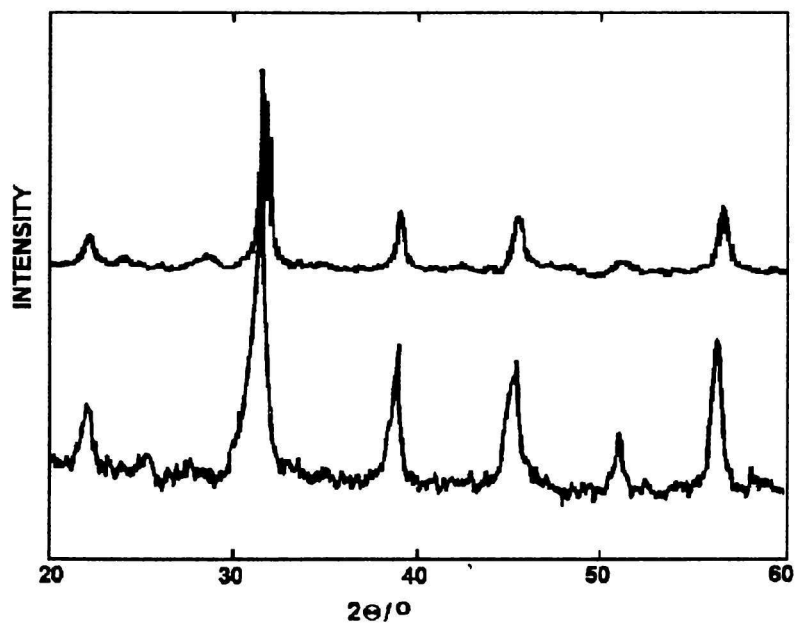


Fig. 6. The X-ray diffraction spectra of the final product obtained by calcination of Ba—Ti hydrogel at 1000°C (lower spectrum) and BaTiO₃ standard (Merck, reagent grade, upper curve).

ceramics on the basis of BaTiO₃, because sintering temperature can be decreased.

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