

# Phase content controlled TiO<sub>2</sub> nanoparticles using the MicroJetReactor technology

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## Abstract

In this paper, a method for the continuous preparation of nanoscaled titania with controlled phase content is presented. The method bases on the MicroJetReactor technology. The synthesis process was carried out by using the hydrolysis of titanium tetraethylate (TET). Synthesis with flow rates to 14 ml/min are implemented, and temperatures are varied between 20 and 210 °C. Particle size distribution measurements by dynamic light scattering (DLS) show monomodal particle size distributions from 1 to 10 nm, stable for more than 24 h. There is no correlation between hydrolysis temperature and the particle size distributions.

XRD (X-ray diffractometry) investigations showed, that crystal structures of anatase, brookite, rutile and an amorphous content can be detected in all samples. Quantitative analysis using the Rietveld refinement shows a significant effect of the synthesis temperature on the phase content. The relative phase content of anatase can be raised from 40 wt% up to 75 wt%, accompanied by a loss of all other phases.

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## 1. Introduction

The synthesis of nanoparticles has been investigated intensively during the last years. Due to the high surface area to volume ratio, these materials are particularly interesting in catalysis. An important kind of catalytic nanoparticles are TiO<sub>2</sub> crystallites, which can be obtained in three different crystal forms (anatase, brookite, and rutile). Besides the well-known photocatalytic activity of anatase, recent results show, that phase mixtures like anatase–rutile and anatase–brookite–rutile composite nanocrystals show a remarkable photocatalytic activity.<sup>1</sup> Even a mixture of 38 wt% brookite and 62 wt% rutile without any anatase can be used as a photocatalyst, as Xu and co-workers showed.<sup>2</sup> A possible explanation is, that electrons move from anatase to a lower energy rutile electron hole. Hence, the recombination of electrons and holes of the anatase is hindered causing a higher photocatalytic activity.<sup>3</sup> As Xu presented, the photocatalytic activity depends highly on the phase contribution

of the TiO<sub>2</sub> material (anatase–brookite–rutile). These examples demonstrate the necessity of synthesis methods controlling the phase content.

TiO<sub>2</sub> nanoparticles can be prepared starting from titanium containing molecules by using methods like flame pyrolysis of alkoxy precursors,<sup>4</sup> and solution methods. Different kinds of titanium compounds are used as a precursor, for example salts like titanium sulfate,<sup>5</sup> halides like TiCl<sub>4</sub> or TiCl<sub>3</sub>,<sup>1,2,6–9</sup> and different alkoxides of the Ti(OR)<sub>4</sub> type.<sup>10–15</sup>

Lee<sup>6</sup> succeeded to prepare pure brookite nanoparticles with a diameter of 10–100 nm by hydrolyzing TiCl<sub>4</sub> in a water/isopropanol mixture followed by reflux crystallization of 20 h at 81 °C. A pure rutile, however, can be achieved by neutralization of a TiCl<sub>3</sub> solution with ammonia followed by drying overnight and a calcination step at 200 and 300 °C, respectively, as reported by Ref. 1. The same group produced mixtures of different titania crystal phases by long-term hydrothermal growth processes.

Di Paola et al.<sup>7</sup> obtained nanocrystals by hydrolysis of TiCl<sub>4</sub> in hydrochloric acid solutions of different concentrations, and NaCl solution at increased temperatures for several hours. A result of the investigations was, that the reaction time as well

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as the concentration of the hydrolysis solutions are the most effecting factors of the synthesis with regard to the crystal phase contribution. Rutile was formed in concentrated as well as in diluted HCl solutions, while the content of brookite depends on the acidity of the solution. Ternary mixtures contenting anatase, brookite, and rutile, however were obtained if the precursor was hydrolyzed with NaCl.

Regarding the formation of HCl during the synthesis, titanium alkoxides are easier to handle and less harmful than  $\text{TiCl}_4$ . Reyes-Coronado hydrolyzed titanium tetraisopropoxide (TTIP) with a small amount of water in 2-propanol. The obtained amorphous product underwent a solvothermal process in aqueous acetic acid or hydrochloric acid, respectively. Brookite was the product of a procedure carried out in diluted hydrochloric acid, while higher concentrations lead to the formation of rutile. The crystallization of anatase only took place in diluted acetic acid. The obtained crystallites show different sizes (anatase up to 6 nm, rutile up to 40 nm, brookite up to about 10 nm).<sup>11</sup>

Garcia-Ruiz et al. describe a hydrothermal synthesis of  $\text{TiO}_2$  starting with titanium tetrabutoxide and hydrochloric acid. They showed that the phase content depends as well on the  $\text{H}_2\text{O}/\text{HCl}$  molar ratio as on the temperature during the hydrothermal treatment.<sup>12</sup> The increase of the  $\text{H}_2\text{O}/\text{HCl}$  molar ratio and the hydrothermal synthesis temperature caused a decrease of the rutile to brookite ratio. Anatase, however, can only be found at a water–acid ratio of 40 and 50, respectively.

A precursor showing much higher reactivity than titanium tetraisopropoxide and -butoxide is titanium tetraethoxide. In spite of this, an autoclave process is necessary to prepare anatase particles with a diameter of 5–10 nm.<sup>16</sup> A semi-continuous process using titanium tetraethoxide and ammonia as catalyst is presented by Park.<sup>17</sup>

In general, the water content of synthesis solutions, the temperature and duration of the solvothermal process, and the time and temperature of the calcination step seem to be the parameters

being efficient in controlling the phase content of  $\text{TiO}_2$  nanoparticles. This means, that nanoscaled  $\text{TiO}_2$  with a noticeable crystallinity can only be obtained by a long-term temperature treatment. The phase content can be controlled by varying the parameters mentioned above.

As well the time factor and the calcination step at all can be deleted by using a method basing on a MicroJetReactor described by Penth<sup>18</sup> and R ufer.<sup>19</sup> This opened the possibility to prepare titania nanoparticles with different phase content by varying educt temperature, and flow.

## 2. Materials and methods

Titanium tetraethylate, titanium tetraisopropylate, 2-propanol obtained from Sigma–Aldrich and nitric acid (65 wt%) from Roth were used as received. 250 ml solutions of 0.5 M nitric acid in water and 0.1 M of the titanium alkoxide precursor in 2-propanol, respectively, were prepared and filled into PE beakers.

The synthesis was carried out using a MicroJetReactor from Synthesechemie GmbH, Lebach, Germany as described by Penth in Ref. 18. Shortly, the reactor is a chamber of stainless steel with 2 face-to-face positioned nozzles of a diameter of 50  $\mu\text{m}$ , and, further, inlet and outlets positioned orthogonal in relation to the nozzles, as presented in Fig. 1.

The reactor chamber is connected to flow controlled high pressure pumps using stainless steel tubings. The steel tubings are wrapped with a heating hose connected to a controller allowing the application of temperatures up to 210  $^\circ\text{C}$  in order to vary the temperature of the educts. Temperatures presented here are the temperatures of the heating hose. Further, the reactor is connected to a nitrogen flask.

The educt solutions were pumped through the steel tubings and the micro-nozzles into the collision chamber. The high velocity of the jets causes that the point of collision lies out-

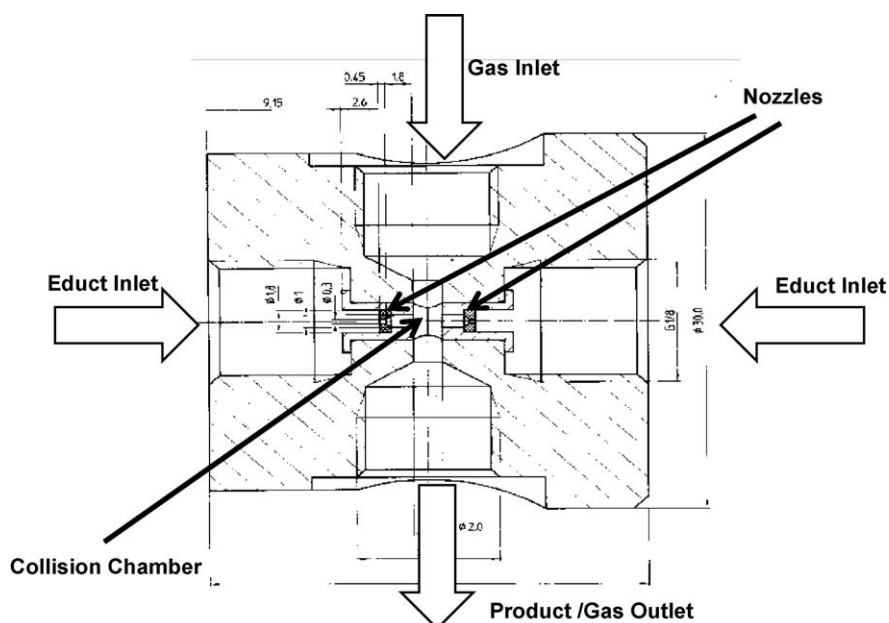


Fig. 1. Drawing of the MicroJetReactor, from Ref. 20.

side the tubes in the middle of the reactor chamber. In this way, a precipitation in the tube system leading to blockage and back-pressure is avoided. A nitrogen gas jet transports the products in situ out of the reactor.

Using the described technology, an ongoing reaction of the formed crystallites with the pre cursor (as in batch processes) is disabled.

The liquid educts were brought into the reactor with 4, 6, 8, 10, 12, and 14 ml/min. The temperature was varied in the following steps: Room temperature and 60, 80, 100, 120, 140, 180, and 210 °C.

Particle size distributions of the suspensions were obtained by dynamic light scattering of the unmodified product suspension using a Malvern Zeta-Sizer device. Dried samples were prepared by dipping a carbon coated copper grid into the suspension, or drying the suspensions in air at room temperature. XRD experiments of the dried powders were performed at CEST (Wiener Neustadt) on an X-Pert powder diffractometer (PANalytical, Netherlands) using Cu K $\alpha$  radiation in Bragg–Brentano geometry at 40 kV and 30 mA, and a silicon single crystal as a sample holder. This device is equipped with a secondary graphite monochromator, automatic divergence slits, and a scintillation counter.

The Rietveld refinement method was used to analyse the XRD measurements. The TOPAS V3 software for powder diffraction data was used for the evaluation.<sup>21</sup>

### 3. Results and discussion

Nanoparticle suspensions with a solid content of 0.4 wt% can be obtained. The described synthesis lead to transparent, weakly yellowish suspensions.

#### 3.1. Variation of the flow rate

The influence of the flow rate on the particle size distribution was investigated at first by dynamic light scattering of the suspensions, and number-weighted evaluation. A result was, that the diameter of the nanoparticles is in a range of 1–10 nm. Particles generated by using a flow rate of 4 ml/min showed a maximum of the distribution at 7 nm, however, particles obtained at higher flow rates show maxima between 2 and 4 nm. There is no trend visible showing a correlation between the flow rate and the particle size, as shown in Fig. 2a. This means, that the input of kinetic energy caused by the high-speed injection leading to the atomization of the educt solution is not a significant factor for the particle size. However, preliminary experiments showed that flow rates below 4 ml/min cause polymodal particle size distributions with no reproducibility. The synthesis process is not stable in this range of flow rate.

After 24 h of aging, there was no difference between the diameters of the particles generated at different flow rates (Fig. 2b). No agglomerates were formed, no sedimentation occurred, but existing agglomerates seems to be dispersed to primary crystallites. Origin is the relatively high molar ratio of TiO<sub>2</sub>:acid of 1:5. The particles are electrostatically stabilized in spite of the high content of ethanol in the suspension. Nitric acid has

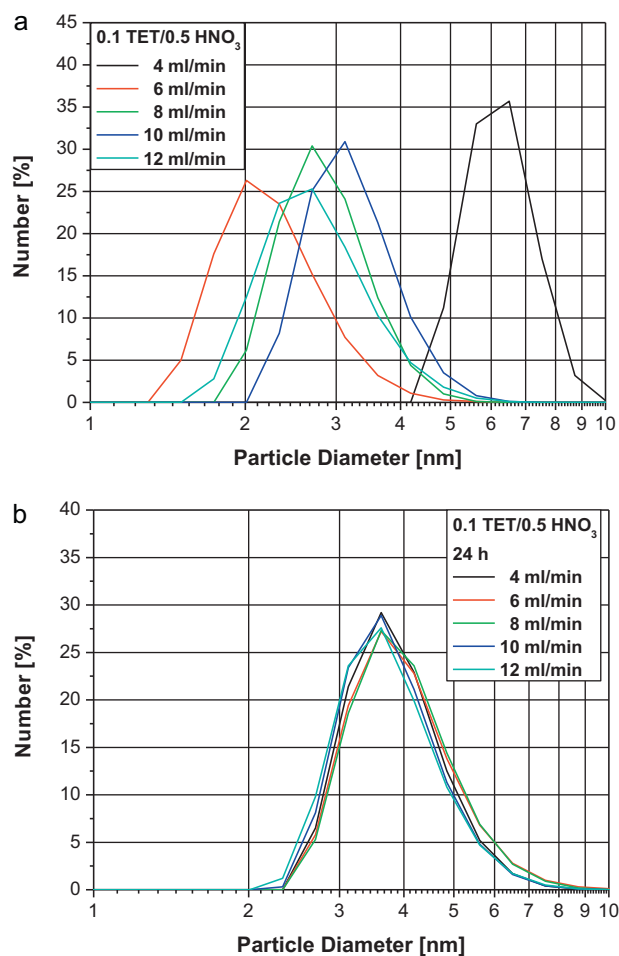


Fig. 2. (a) Particle size distribution of suspensions prepared from TET at different flow rates. (b) Particle size distribution of suspensions prepared from TET at different flow rates after 24 h.

two different functions in the process. Firstly, it is the catalyst for the hydrolysis of the titanium alkoxide followed by the formation of the particles. Besides, a second function is the stabilization of the resulting suspensions. This helped to avoid the use of dispersing agents like polyethercarboxylates as Rüfer used one to stabilize the BaSO<sub>4</sub> nanoparticle suspensions obtained by a MicroJetReactor approach from barium chloride and potassium sulfate as the educts. He succeeded in producing particle sizes of 71–168 nm.<sup>19</sup> The long-term stability of the suspensions is an important property with respect to later applications.

A Rietveld refined XRD analysis was carried out leading to the results presented in Figs. 3 and 4. Anatase crystallites have an average size of 2–3 nm, brookite crystallizes in the range of 1–2 nm. Rutile however, forms crystallites in the dimension of about 10 nm. The XRD based crystallite size analysis was in accordance to the DLS results presented in Fig. 2. The results from XRD data calculations confirmed that the primary crystallites were electrostatically stabilized in the product suspensions, and no agglomeration took place.

Furthermore, Rietveld refinement was used to get an insight in the phase behaviour with regard to the flow rate. The rela-

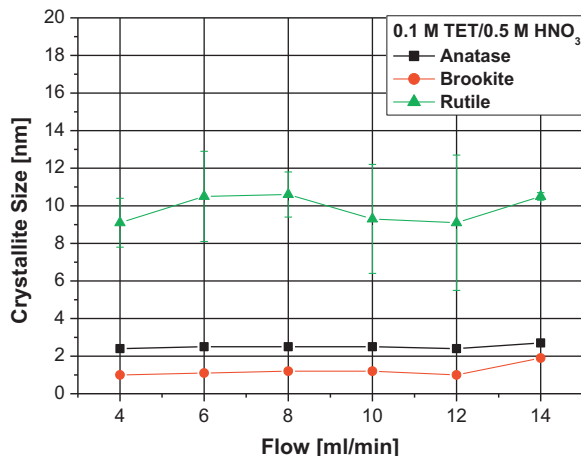


Fig. 3. Crystallite size from XRD data versus flow of powders prepared from TET at different flow rates.

tive phase contribution (Fig. 4) at all is marked by a very low content of rutile and amorphous matter (below 10 wt%). An increase of the rutile as well as the amorphous part up to about 10 and 15 wt%, respectively, can be observed if the flow rate is higher than 12 ml/min. The brookite content was between 50 and 60 wt%, and decreased to 40 wt% above a flow rate of 12 ml/min, accompanied by anatase which decreases from a range of 40 to 50 wt% to 35 wt% within the same flow rate values. Above 12 ml/min there seems to be a change in the mechanism of particle formation. It is noticeable, that there is a gain of the amorphous matter in spite of a higher energy input. Obviously, the higher mixing velocity combined with a faster atomization of the liquid stops the crystallization before the critical crystallite size is reached. It should be expected, that the crystallinity rises with an increasing amount of energy. Kanna reported about mixtures of anatase, rutile and mainly amorphous  $\text{TiO}_2$  when the synthesis is carried out as a simple precipitation without a heat treatment step (lower energy input). Nevertheless, the mixtures showed a photocatalytic activity.<sup>22</sup>

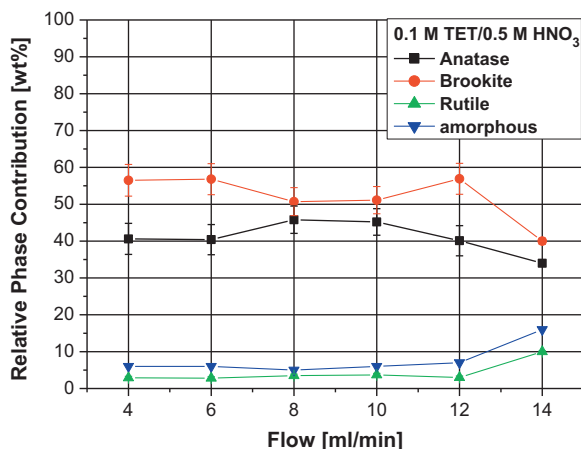


Fig. 4. Relative phase contribution versus flow of powders prepared from TET at different flow rates.

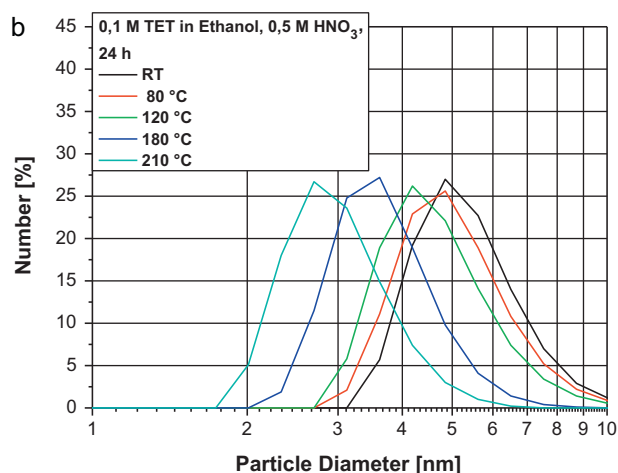
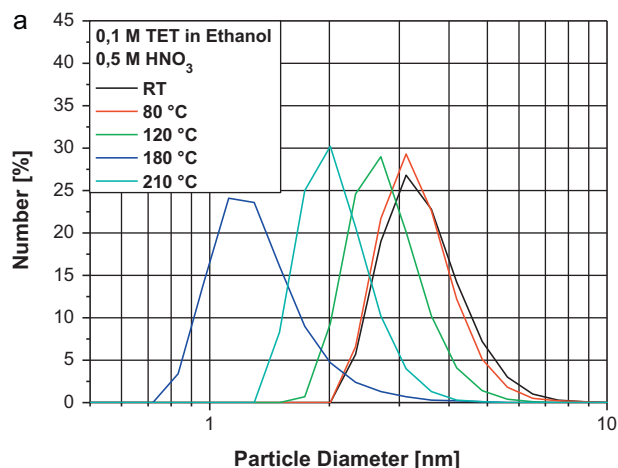


Fig. 5. (a) Particle size distribution of suspensions prepared from TET at different educt temperatures. (b) Particle size distribution of suspensions prepared from TET at different educt temperatures after 24 h.

### 3.2. Variation of the educt temperature

Using the heating equipment described above, the educt temperature was varied at a constant flow rate of 14 ml/min. The particle size distributions of the suspensions are presented in Fig. 5a and are in the range of 1–10 nm. There was a weak trend to a diminishment of the particle size as a consequence of an educt temperature raise. After 24 h, there was no sedimentation and no significant change of the particle size. In Fig. 5b, the distributions are documented, and the trend described above is still visible. Comparable to the behaviour of the systems described under Section 3.1 (Fig. 2), the suspensions were stable for 24 h due to the electrostatical stabilization. Regarding that the chemical composition of the educts and products were the same, the very similar colloidal behaviour is an indication for the effect that the surface chemistry of the crystallites was not influenced significantly by the educt solution temperature.

The low influence of the educt temperature on the crystallite size was also revealed from the data extracted from the XRD measurements (Fig. 6). A Rietveld refinement was helpful to come to the diagram of Fig. 7. Anatase and brookite crystallites were of about 2 nm without any trend in relation



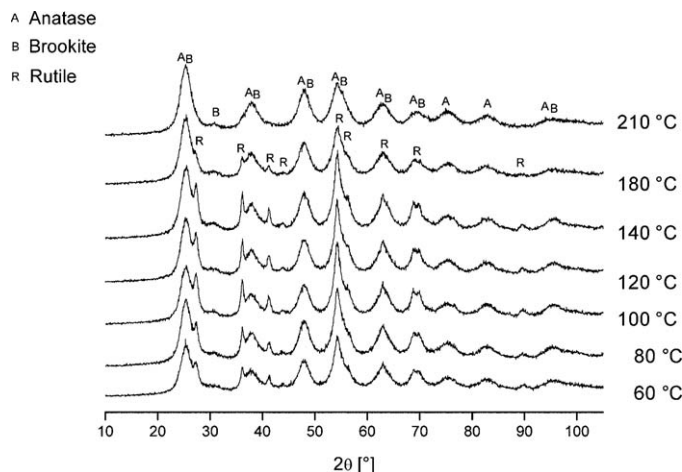


Fig. 6. XRD plot of powders obtained at different educt temperatures.

to the educt temperature. The size of rutile crystallites obtained at room temperature was 11 nm, however, with the ascending educt temperature, the crystallite size decreases quickly to values between 6 and 8 nm. The drop of the rutile crystallite size caused the obvious weak trend to smaller particles in Fig. 5. A comparable ranking of crystallite sizes of the three polymorph phases was presented by Reyes-Coronado by investigating the hydrodynamic diameter of particles synthesized by a hydrothermal process from DLS measurements. Particles between 35 and 240 nm were obtained, and the difference can be explained by a different bias to agglomeration.<sup>11</sup> In opposite, as the Rietveld refined XRD data prove, the particles are no agglomerates. A temperature dependent growth of titania crystals analysed via the Lifshitz–Slyozov–Wagner-model, and an Arrhenius-plot was introduced by Oskam.<sup>13</sup> The results show that it is not possible to transfer the principals of the long-term temperature treatment based synthesis processes to the MicroJetReactor technique.

However, there is an articulate effect of the educt temperature on the crystal structure. The (1 0 1) diffraction peak of anatase

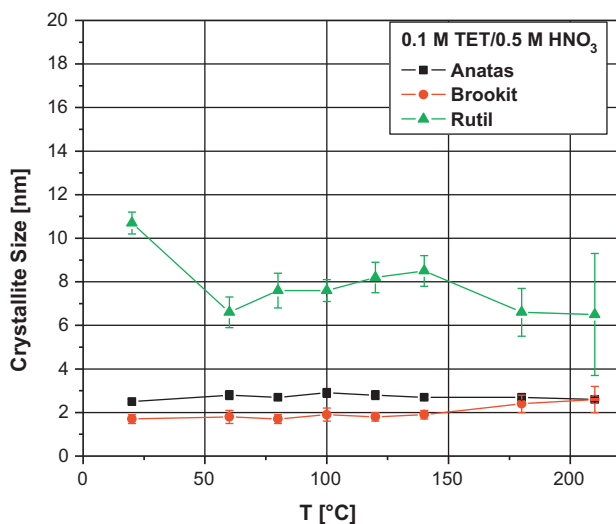


Fig. 7. Crystallite size from XRD data versus educt temperature of powders prepared from TET.

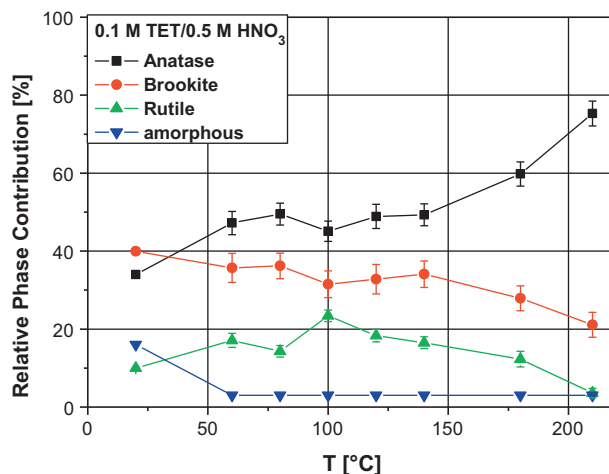


Fig. 8. Relative phase contribution versus educt temperature of powders prepared from TET.

( $2\theta = 25.28^\circ$ ) in Fig. 6, overlaps both with the (2 1 0) and the (1 1 1) peak of brookite ( $2\theta = 25.34^\circ$  and  $25.69^\circ$ ),<sup>7</sup> the brookite peaks disappear more and more during an increase of the anatase peak. Another interesting effect is the increase and decrease of the (1 0 1) diffraction peak of rutile at a  $2\theta$  of  $36.15^\circ$ <sup>23</sup> with the rising educt temperature. A deeper insight was done using the Rietveld refined data. Fig. 8 presents the relative phase contribution of the titania powders prepared at different temperatures. The content of anatase was raised from 34 to 75 wt% by rising the temperature of the educt solutions from room temperature up to 210 °C. The same temperature shift caused the decrease of the brookite content from 40 to 20 wt% by weight. The phase behaviour with regard to rutile is interesting because the content was 10 wt% at room temperature and about 25 wt% as a maximum. A powder produced at a synthesis temperature of 210 °C possessed only 4 wt% of rutile. The Rietveld refinement also certifies the performance of the (1 0 1) diffraction reflex of rutile when the synthesis temperature became higher. Further, the amorphous part sank from 16 wt% at room temperature to 3 wt% at 60 °C. No change in amorphous contribution can be observed when the educt temperature was shifted. A decrease of amorphous phase means an increase of the crystallinity at all, what also was attested by selected area electron diffraction.

#### 4. Conclusions

Crystalline nanoscaled titania can be prepared by using a MicroJetReactor plant without hydrothermal or calcination heat treatment steps from the molecular precursor titanium ethoxide. The synthesis parameters were the flow rate and the temperature of the injected educt solutions. The primary crystallite size was between 1 and 10 nm and there was no correlation neither to the flow rate nor the educt solution temperature. Stable suspensions were obtained. The crystal phase contribution was not significantly influenced by the flow rate, however strongly by the educt temperature. An increase of the temperature to 210 °C caused a dramatically ascent of the anatase content from 34 to 75 wt%.

The method presented here enables the continuous production of titania nanocrystallites with a defined relative phase contribution. The crystallization is effected by the kinetic energy of the liquid jets colliding in the reactor chamber. The time for the contact of both the solutions is very short. This is the explanation for the very small particles: Short after the start of the crystallization, it is interrupted by the blow-out of the nitrogen jet. However, this is only possible at low precursor concentrations. In this case, the precursor reacts completely and no further hydrolysis followed by crystallization can occur in the suspension.

Further investigations will show the influence of the different phase compositions on the photocatalytic activity of the powders.

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