

# FABRICATION OF AGGLOMERATE-FREE NANOPOWDERS BY HYDROTHERMAL CHEMICAL PROCESSING

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## ABSTRACT

A chemical processing technique for the fabrication of nanopowders has been developed. The route is based on precipitation processes in solutions, either within aqueous droplets in micro-emulsions in the presence of surface modifiers like surfactants or by direct precipitation in solutions in the presence of these surface modifiers or small organic molecules directly bonded to the particle surface. In order to obtain well crystallized or densified particles, a continuous flow hydrothermal process has been developed which allows the fabrication of agglomerate-free surface modified nanopowders. The surface modification provides a full redispersibility after drying and permits a water-based processing. Nanoparticles preparation for  $ZrO_2$ , ITO and ATO by this route are described.

## INTRODUCTION

The interest in nanopowders has constantly increased over the past years for scientific as well as for industrial reasons. This is based on the early work of Gleiter, who stated that nanostructured ceramic materials may have extraordinary properties, such as plastic deformation abilities [1, 2]. Meanwhile, various methods have been developed for the preparation of ceramic nano-scale powders, mainly based on gas phase reactions such as vapor phase condensation, chemical vapor condensation [3] or chemical vapor reaction [4]. In addition, plasma pyrolysis [5, 6, 7, 8] or laser ablation processes have been investigated [9, 10, 11, 12]. Another method for the fabrication of nanoparticles are precipitation processes from homogeneous solutions as a typical chemical bottom-up process. Chemical precipitation processes are well established for the fabrication of a huge variety of materials. The process, in general, is initiated by a nucleation step followed by a growth reaction [13, 14]. If the precipitation is carried out in very diluted solutions, as shown by Matievic [15], small particles in the nano range can also be produced by this route. One of the major drawbacks of the wet chemical process is that almost all precipitates show a rather high surface reactivity, mainly caused by residual surface groups, such as metal ion bonded OH groups or others. Due to their high surface small nano scaled particles generally show a strong interaction. If the particle size, as a result of the growth process, reaches the  $\mu\text{m}$ - or the  $10\text{-}\mu\text{m}$  state, weak agglomerates can be separated by mechanical forces like milling or grinding. Usually, this is not possible in the nano range, which means that nanoparticles after precipitation have to be protected on their surface in order to avoid agglomeration. The simplest way of protecting them from approaching each other is to use electric charges, e.g. by establishing an appropriate pH value. The use of electric charge stabilization is the typical method applied by the so-called classical sol-gel process, which means that the fabrication of stable sols is generally carried out by this mechanism [16]. The aim of this paper is to show how the use of a surface modifier during the production process leads to agglomerate-free redispersible powders even through a continuous flow chemical process, and how a broad sintering regime is observed.

## GENERAL ASPECTS

Surface charge stabilized sols have been used for the fabrication of thin coatings, mainly on glasses. Due to the small particle size of the sols, which is in the lower nm range [17], transparent coatings can be obtained. SiO<sub>2</sub> and other inorganic coatings have been focused upon by numerous authors, especially for coatings on glass. Despite widespread activities in research, only a few industrial processes related to investigations have been developed so far. The fabrication of monolithic ceramics using sols has been investigated, but monolithic processing was rather unsuccessful because the fabrication of large-scale solids from sols is suffering from low solid content gels and green body gels which, due to their weakness combined with high shrinkage rates, are extremely difficult to be dried. The solidification of sols to gels is the crucial point in sol-gel nanoprocessing. If the electric charges in electrostatically stabilized sols are 'removed', a very fast gelation process takes place with uncontrolled interaction between the sol particles, leading to a high concentration of defects and pores with a broad size distribution. This in turn leads to inhomogeneous sintering, and large pores can be closed only at higher temperatures. So the benefits of the nanoparticles cannot be exploited in the monolithic ceramic sol-gel processing and an undesired broad sintering range is obtained. This is schematically shown in fig. 1.

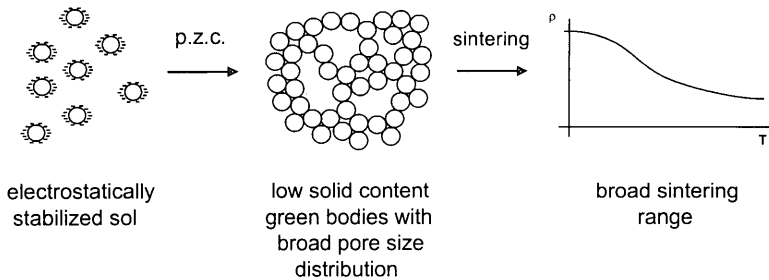


Fig. 1: Scheme of the typical sol-gel nanoparticle processing to parts.

Based on these considerations, alternative concepts have been developed for substituting electric charge stabilization by surface modification, as described in [18, 19, 20]. If molecules containing small functional groups are used to block the surface during or after the growth process, particle size, particle size distribution and particle interaction can be controlled easily. Moreover, if these small molecules are bifunctional, specific 'chemical reactivities' can be bonded to the particles' surface, influencing its chemical reactivity, its  $\zeta$ -potential and, of course, its further processing properties. This is schematically shown in fig. 2.

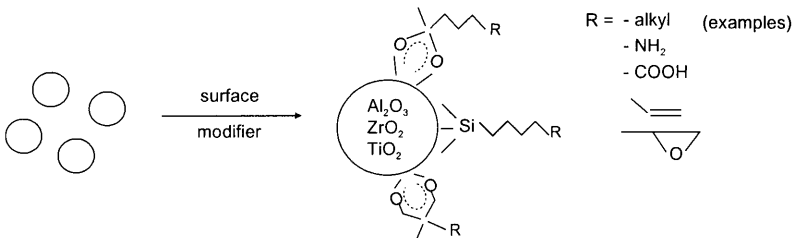


Fig. 2: Basic principle of a surface modification; examples for modification.

Relatively small molecules have to be used if the organic content of these systems shall be low, which might be of importance if ceramic processing is envisaged. This, in general, forbids the use of polyelectrolytes for stabilization, which are widely used in ceramic processing for powders with particle sizes in the  $\mu\text{m}$  range. The advantage, however, of surface modifiers of the polymer type is their perfect bonding to many inorganic surfaces. In order to keep the modifying molecules on the surface, specific bonds to the surface have to be used, but, as shown elsewhere [19], the chemical bond principle known from solution chemistry (salt and complex formation) can be used on the nanoparticles' surface. This means that a wide variety of monomeric, oligomeric and polymeric modifying components are available for the surface modification of nanoparticles. An interesting method may be the perfect surface coverage of oligomeric systems with the low organic content of small molecules. In this case, an exchange has to be carried out during processing.

For the preparation of larger amounts of surface stabilized powders, other aspects have to be taken into consideration, for example, the fabrication of well-crystallized particles, which normally is not the case in a complete way if one considers classical sols (alumina, titania or zirconia), which, in general, are only partly crystallized after fabrication. Other aspects are cleaning processes, separation processes and drying techniques to avoid agglomeration. In this paper, a route is described to prepare ceramic nanopowders by using different types of surface modifiers to obtain well-crystallized powders.

## EXPERIMENTAL

### Powder synthesis

#### $(\text{Y}_2\text{O}_3)/\text{ZrO}_2$

For the fabrication of zirconia powders, 255 g Zirconium-n-propoxide were dissolved in 200 ml of ethanol. This solution was slowly added to 200 ml of an aqueous solution of 7,6 g oleic acid polyethyleneoxide ester ( $\{\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2[(\text{CH}_2)_2\text{O}]_{20}\}$ , OPE), and 20 ml of 25 wt.% aqueous ammonia solution were added to establish a pH value of 11. For Y containing systems,  $\text{Y}(\text{NO}_3)_3$  was added to the ethanolic solution. The sol formation was completed after stirring for 3 h at 20 °C. The prepared sol was placed into an autoclave and was treated at 230 °C and 70 bar for 3 h. Afterwards, the suspension was flocculated by pH adjusting to pH = 5,9 with 20 ml of 1 n HCl, the point of zero charge of the prepared, modified particles and the solid was separated by filtration. In order to remove soluble reaction products, the resulting sediment was repeatedly diluted with 1 l of deionized water, flocculated by pH-adjusting to pH = 5,9 and again filtrated until the conductivity of the washing water was below 5  $\mu\text{S}$ . Finally the powder was dried at 60 °C and 20 mbar.

#### $\text{SnO}_2/\text{Sb}_2\text{O}_3$

81,25 g of  $\text{SnCl}_4 \cdot 5 \text{H}_2\text{O}$  and 2,66 g  $\text{SbCl}_3$  (5 mole % with respect to Sn) were dissolved in 200 ml of ethanole. This solution was slowly added to 200 ml of an aqueous solution of 3,5 g OPE and 35 ml of aqueous ammonia (25 wt.%), the pH was 14. After stirring for 3 h at 20 °C, the resulting sol was hydrothermally treated at 150 °C and 10 bar for 3 h. The resulting reaction product was treated as described above.

#### $\text{SnO}_2/\text{In}_2\text{O}_3$

110 g of  $\text{InCl}_3$  and 14,1 g  $\text{SnCl}_4 \cdot 5 \text{H}_2\text{O}$  (8 mole % with respect to In) were dissolved in 250 ml of deionized water and than slowly added to 200 ml of an aqueous solution of 7 g OPE 35 ml of aqueous ammonia (25 wt.%), the pH was 14. The sol formation was completed after stirring for 5 h at 20 °C. After hydrothermal treating at 360 °C and 160 bar for 5 h crystallinity was achieved. The resulting reaction product was treated as described above.

## Exchange of the Surface Modifier

In order to exchange the OPE bound on the particles' surface, 50 g of the powders were suspended in 200 ml of 8 n NaOH and 200 ml toluene were added and stirred for 5 h to extract hydrophobic reaction products. The mixture was heated under reflux for 5 h ('deesterification'). After the deesterification the solid was separated after the pH value of the aqueous suspension was adjusted to pH = 7 to flocculate the precipitate (point of zero charge of  $ZrO_2$ ) by centrifugation (4000 r/min, 15 min). In order to remove soluble reaction products, the resulting sediment was repeatedly diluted with 1 l of deionized water, filtrated and washed until the conductivity of the washing water was below 5  $\mu$ S. 4 g of trioxadecanic acid (TODS) were added to the resulting suspension as surface modifier. After stirring for additional 3 h the pH of the suspension was adjusted to pH = 8 (point of zero charge of the TODS-modified  $ZrO_2$ ), and the flocculated powders were washed as described above in order to remove excess TODS not bound onto the particles' surface. Finally, the powder was isolated by filtration and dried (60 °C, 20 mbar, 5 h). The synthesized powders were characterized by HRTEM, x-Ray, IR spectroscopy, and laser backscattering.  $\zeta$ -potential measurements were carried out in aqueous suspensions (solid content: 1 wt.-%) by titration with 0.1 n NaOH and 0.1 n HCl, respectively.

## RESULTS

In order to avoid agglomeration during the precipitation of nano-scale modified  $ZrO_2$  particles the reaction was carried out in presence of the surface modifying agent OPE as described above. This molecule is rather large, but it has been selected because of its ability to prevent agglomeration. For further processing to ceramics, the organic content is too high, so a second step to remove the ester has to be taken into consideration. The precipitates were analyzed by X-ray diffraction, TEM, IR spectroscopy, and the particle size distributions were also measured. As shown in fig. 3a, the particles are rather amorphous after precipitation. From TEM investigations, not shown here, the size of the amorphous precipitates can be roughly estimated to be in the range of 5 - 10 nm. The particles can easily be dispersed in water at pH 8 and the size distribution is shown in figure 3b. The particle size is in the nm range with a narrow distribution where 90 % of the particles are smaller than 30 nm.

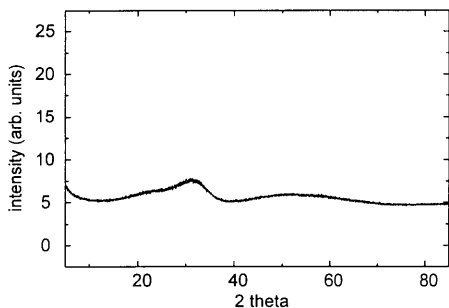


Fig. 3a: X-ray diffraction patterns of  $ZrO_2$  nanoparticles coated with OPE after precipitation.

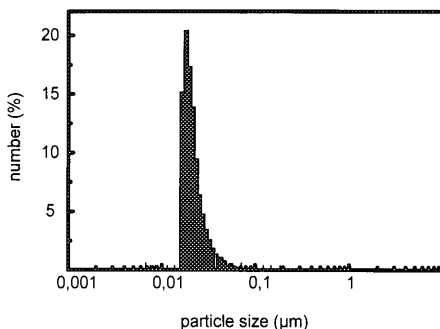


Fig. 3b: Laser backscattering measurement of the distribution of  $ZrO_2$  nanoparticles coated with OPE in  $H_2O$  as solvent at pH = 8.

In order to obtain a better crystallinity, a solvo-thermal treatment seemed to be an interesting option. It is a well-known fact that inorganic precipitates can be recrystallized under hydrothermal conditions (mixture of EtOH and H<sub>2</sub>O). The interesting question here was how far the OPE survives the solvo-thermal process and to what extent it maintains its protective function during this solvo-thermal process. For this reason, an IR spectrum was taken from the powder covered with about 10 wt.-% of the OPE before the treatment (fig. 4).

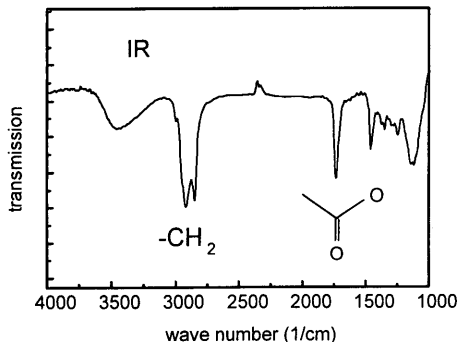


Fig. 4: IR-spectrum of ZrO<sub>2</sub> nanoparticles coated with OPE as received after precipitation.

The carboxylic frequency of the ester can be easily identified. After the hydrothermal treatment, the X-ray diffraction pattern of the zirconia containing 8 % of yttria (fig. 5) clearly shows the cubic modification, which can be attributed to the solvo-thermal treatment.

The IR spectrum of the washed powder (fig. 6) shows that the ester on the zirconia particle remains completely unchanged.

The particle size is still in the range of 5 - 10 nm, as shown by HRTEM investigations (fig. 7) as well as by laser backscattering (fig. 8). This means that first, the selected OPE survives the solvo-thermal process without decay and second, that the particle size remains almost unchanged, meaning that no agglomeration or detectable grain growth has taken place.

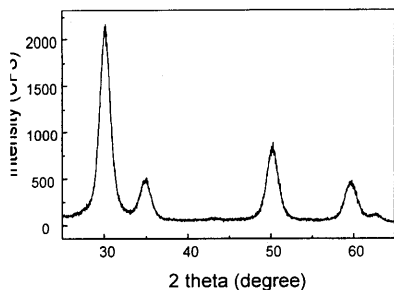


Fig. 5: X-ray diffraction spectrum of Y<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> after hydrothermal crystallization (230 °C, 70 bar, 3 h).

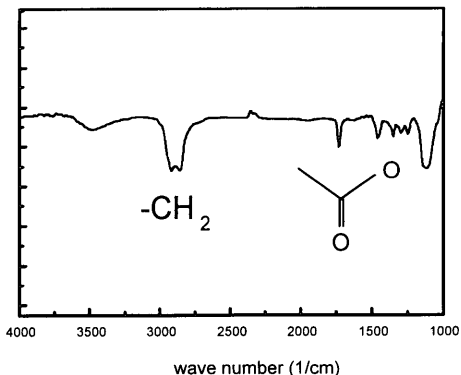


Fig. 6: IR-spectrum of the washed ZrO<sub>2</sub> nanoparticles coated with OPE after hydrothermal crystallization at 230 °C, 70 bar, 3 h.

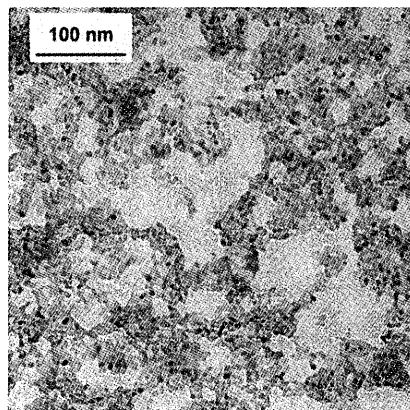


Fig. 7: HRTEM micrograph of 8-Y<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> after hydrothermal crystallization (230 °C, 70 bar, 3 h), surface modifier: OPE.

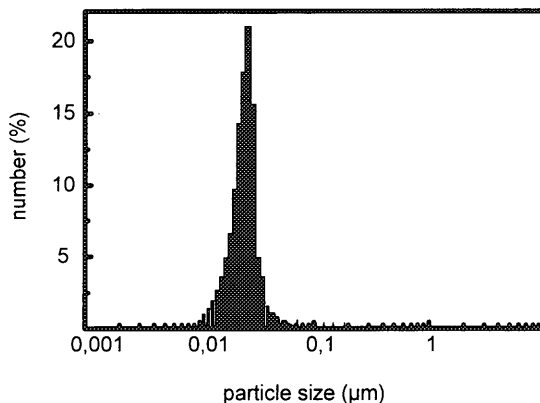


Fig. 8: Laser backscattering measurement of the distribution of crystallized and washed ZrO<sub>2</sub> nanoparticles coated with OPE in H<sub>2</sub>O as solvent at pH = 3.

Different techniques were investigated to substitute the polymeric ester. The direct treatment of the ester-coated particles with short-chain molecules like  $\beta$ -diketones or carboxylic acids, was unsuccessful. This is due to the strong bound of the polymeric ester to the particle surface. The treatment of the system with sodium hydroxide, however, led to a complete removal of OPE from the surface. After the NaOH treatment, precipitating the nanoparticles by flocculation at the point of zero charge and washing the system to neutral, the addition of carboxylic acids led to a short-chain molecular coating. In fig. 9 the  $\zeta$ -potential curves of the zirconia particles covered with OPE, the zirconia particles after NaOH treatment and washing to neutral as well as after recoating them with trioxadecanic acid (TODS) are shown. The  $\zeta$ -potential curves show clearly the effect of the different reaction steps. Flocculation of the uncoated ZrO<sub>2</sub> takes place at the point of zero charge close to pH7,

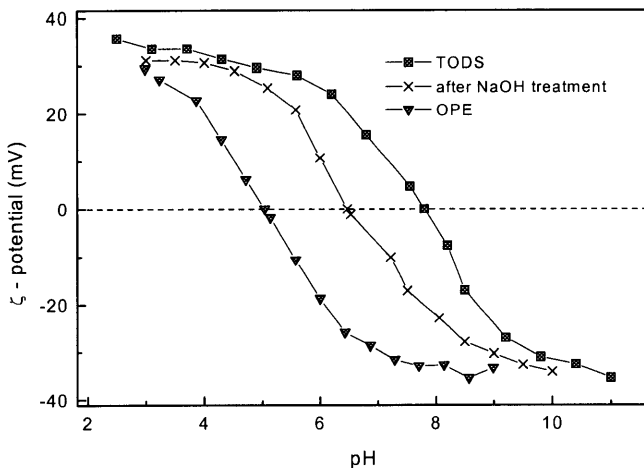


Fig. 9: pH-dependent  $\zeta$ -potential of hydrothermally crystallized  $ZrO_2$ .

i.e. for the NaOH treated and washed precipitates, which can easily be filtered. Flocculation is a step considerably facilitating the separation; otherwise it is extremely difficult to separate nanoparticles from liquids. After drying, these powders are very well redispersible in water, as described elsewhere [19]. In fig. 10 the IR spectrum of the TODS modified yttria/zirconia is shown. It clearly depicts the  $C=O$  frequency of a carboxylate group and not the frequency of the free carboxylic acid. That means that the acid group is bonded to the particle

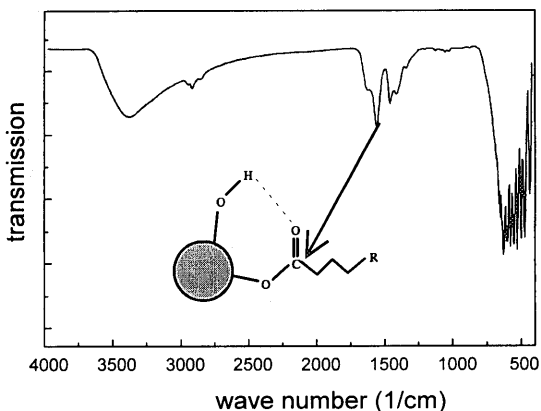


Fig. 10: IR-spectrum of the TODS-modified  $Y_2O_3/ZrO_2$ .

surface. Analytical investigations show that on the average 400 molecules of TODS are absorbed per particle. This leads to a total organic content of about 7.7 wt.-%. Up to now, it has not yet been clearly known why powders modified OPE are less redispersible than the TODS systems.

Based on these investigations, a concept of a process has been worked out, the flow chart of which is shown in fig. 11.

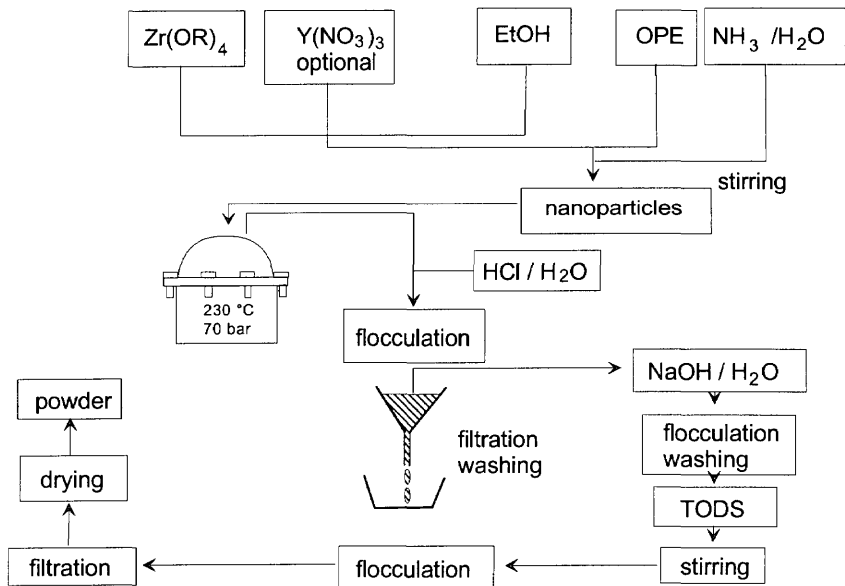


Fig. 11: Flow chart of the process.

All steps of this process consist basically of well-known chemical processing technologies and what seems to be important is that after the autoclave reaction, a water based technology is used. A chemical engineering development has been carried out to change the batch reactor system into a continuous flow reactor system for continuous nanopowder production.

In fig. 12, the scheme of the production line is shown. The core technology part of the system includes a continuous flow hydrothermal reactor tube. This technique has been built up for pilot scale production of zirconia or zirconia/yttria powders at first and was then used for other systems, too. The system consists of several precursor containers (closed system technology). For sensitive systems, the reactions can be carried out under inert gas conditions. The liquids are pumped into the reaction container, stirred for the requested time period and then pumped into the storage container. From the storage container the liquid pumped into a heater where it is heated up to (2) the desired temperature and then pumped continuously into the tube reactor (3). The flow rate is adapted to the requested retention time. In (3) the treated liquid is cooled down, the pressure is relaxed and the flocculation, filtration and the surface modification steps are carried out.



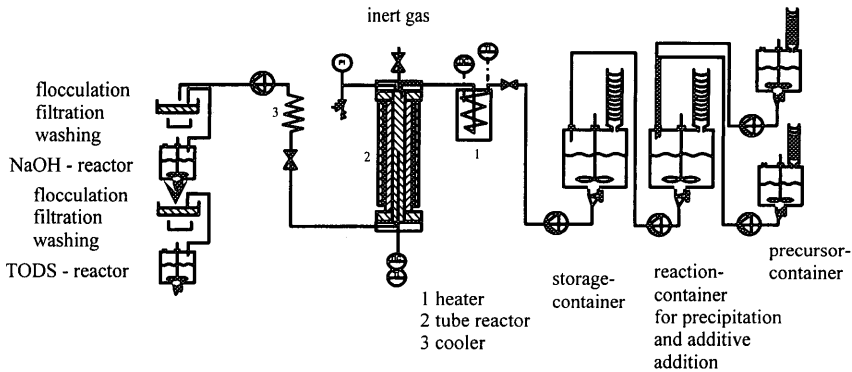


Fig. 12: Flow chart of the continuous flow reactor for the hydrothermal crystallization of nanocrystalline powders in solution [21].

The fabrication of antimony and indium doped tin oxide (ATO or ITO) powders is basically carried out by using the same reaction principles. In fig. 13 the flow chart for the synthesis of ATO or ITO particles is shown.

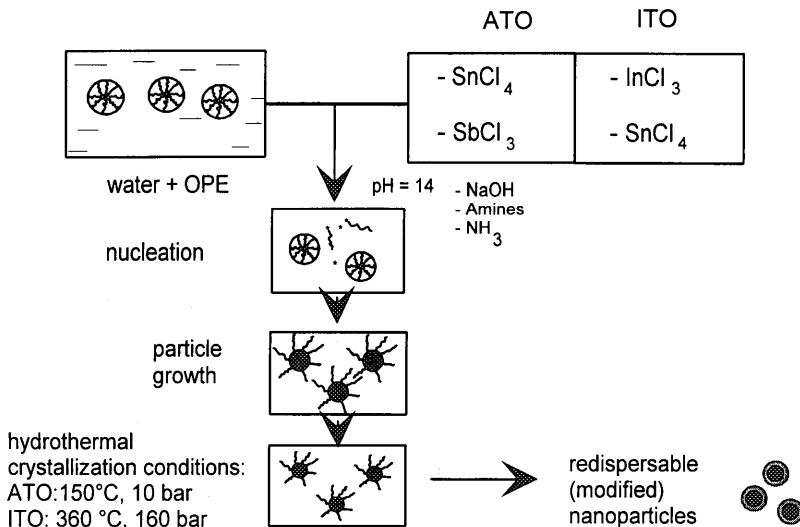
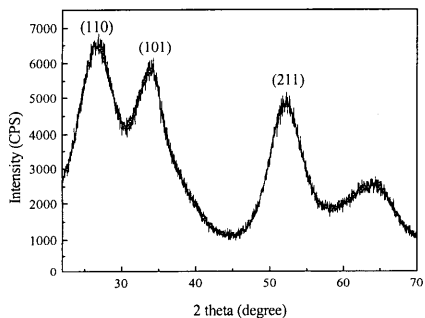


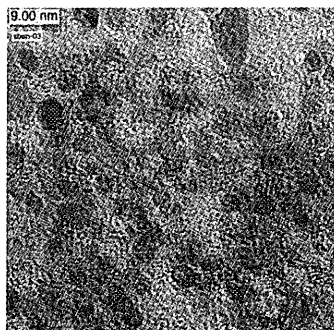
Fig. 13: Flow chart for the preparation of nanocrystalline ATO- and ITO particles.

Only the chlorides have been used as precursors. For both, ATO or ITO, identical processing parameters have been applied. The hydrothermal conditions in this case have been optimized to 150 °C and 10 bar for 4 hrs. In fig. 14 the X-ray diffraction patterns and the HRTEM micrograph of an ATO powder obtained by this process are shown. As can be recognized in the diffraction patterns, the particle size is rather small. In the high-resolution TEM, the particle size can be identified to be between 3 and 5 nm, which is in accordance with the particle size calculated from the diffraction patterns. No high temperature treatment has been carried out so

far with these powders in order to establish appropriate electronic properties. As in the case of  $ZrO_2$ , ITO as well as ATO can be redispersed in  $H_2O$  to fabricate sols for optical purposes.



14a



14b

Fig. 14a: X-ray diffraction of nanocrystalline antimony-doped (5 mole %) tin dioxide. 14b: HRTEM picture of nanocrystalline powder dispersed in water and tetramethylammoniahydroxide. Particle size ranges from 3 to 5 nm. The surface modifier chosen in this case was TODS.

As shown elsewhere [20], these powders can be used for green body fabrication with green densities up to 60 vol.-% with a mono modal pore size distribution in the nm range.  $Y-ZrO_2$  has been densified to full density at temperatures below 1100 °C and due to the narrow pore size distribution very narrow sintering range has also been obtained. This shows the potential of these powders for ceramic processing.

## CONCLUSION

The investigations of using a combination of controlled growth precipitation reactions in the presence of surface modifiers, the solvo-thermal treatment for achieving desired crystallinity and the exchange of ligands in order to obtain suitable processing properties have shown that it is possible to synthesize agglomerate-free well crystallized nanoparticulate powders.

This process can be used for nanoparticle fabrication of various compositions. The use of oligomeric molecules leads to a perfect protection during the precipitation as well as during the solvo-thermal crystallization. This protection is necessary in order to maintain the particle size distribution obtained from the precipitation process. For further processing of the nanoparticles the relatively high amount of organics introduced into the system by the oligomeric compounds may be disturbing. For this reason, it is necessary to remove the genuine coating first by substituting it in a two step chemical process through an electrostatic stabilization (for example, the absorption of sodium ions, protons or others) and then to recoat them with short-chain molecules of the desired type, e.g., carboxylic acids. The carboxylic acid coatings lead to systems that are completely redispersible in water. These nanoparticulate systems can be then used for many purposes, for example for ceramic processing or for coatings, even optical coatings, since the particle size is very small. The advantage compared to conventional sol-gel processing is that the systems can easily be stored in form of dry powders, which is very convenient compared to sol storage. In addition to this, water-based technologies can be used very easily compared to the alcohol-based technologies in the conventional sol-gel processes.

Last but not least, the technology is based on well known chemical engineering processes with the potential to build up continuous flow low cost productions.

## ACKNOWLEDGMENT

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