# Hydrothermal synthesis of nanocrystallite $BaSnO_3$ powders by peptization the precursor $SnO_2 \cdot xH_2O$

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## 1. Introduction

In the last years $BaSnO_3$ has gained much attention as a material for gas sensors [1]. A key requirement for the utilization is a large specific surface area. In contrast to conventional solid state reactions at high temperature leading to large particles [2], hydrothermal synthesis offers the possibility for the production of ultrafine $BaSnO_3$ particles [3]. The objective of this work is to prepare a nanoscaled $BaSnO_3$ powder with a high specific surface area by employing a $SnO_2$ x $H_2O$ sol.

## 2. Experimental procedure

The precursor $SnO_2 \cdot xH_2O$ gel was synthesized through the reaction between ammonia and $SnCl_4$. 25% ammonia solution was added to the washed gel for peptization (pH = 9.3), which converts a gel into a colloid solution. The mixture of peptized $SnO_2 \cdot xH_2O$ and $Ba(OH)_2$ was charged in an autoclave and hydrothermally treated at 250°C for 6h. The product was washed with water until the suspensions pH-value was 7. The powder obtained by drying was calcined at temperatures ranging from 260°C to 330°C and characterized with the x-ray diffractometer (XRD), the thermogravimetry and the differential thermal analysis (TG-DTA), the Fourier transform infrared spectrometer (FTIR), the high resolution transmission electron microscope (HR-TEM), the BET gas adsorption analyzer and the ultrafine particle analyzer (UPA).

## 3. Results

$SnO_2 \cdot xH_2O$ gel prepared by the reaction of $SnCl_4$ in water with ammonia can be peptized if the pH value is adjusted to 8.3 or higher resulting in transparent suspensions (Figure 1).

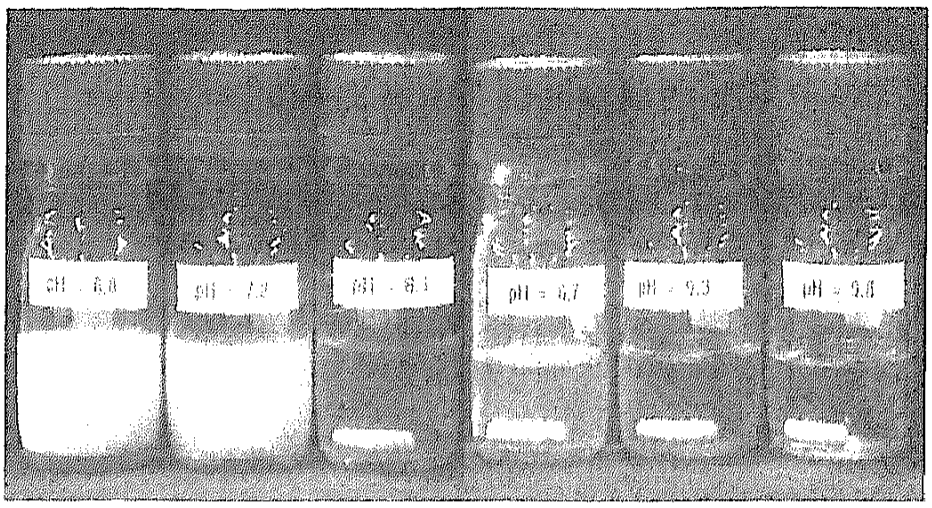
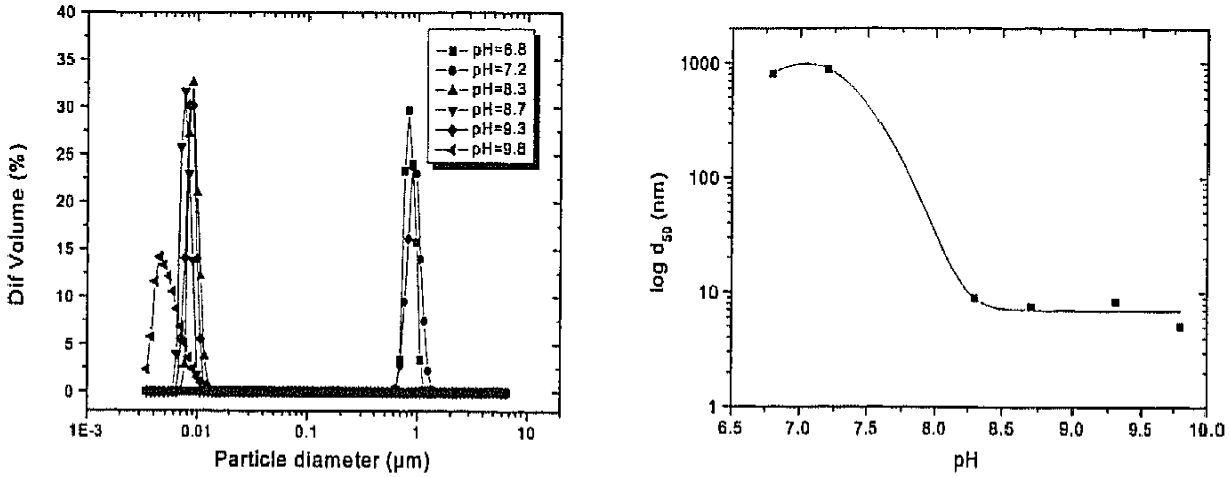


Fig. 1 Tin oxide hydrate peptized with 25% ammonia aqueous solution at different pHs.

Figure 2a illustrates the distribution of particle diameters at different pH values. In the case of the peptized sols particle sizes of less than 20 nm are realizable. As shown in Figure 2b the mean particle size ($d_{50}$-value of the volume distribution) decreased from ca. 0.8 µm to 8 nm by increasing the pH to 9.8.




a b

Fig. 2 (a) Particle diameter contribution, (b) mean particle diameter $d_{50}$ of $SnO_2 \cdot xH_2O$ peptized at different pHs.

The powders synthesized from $SnO_2 \cdot xH_2O$ and $Ba(OH)_2$ by hydrothermal reaction consist of $BaSn(OH)_6$. The particles of $BaSn(OH)_6$ derived from the non peptized $SnO_2 \cdot xH_2O$ gel are strongly agglomerated and the resulted clusters are larger than 1 µm (Figure 3a). These agglomerates are formed of many overlapped crystallites with a diameter of 10 to 50 nm. In contrast to this, $BaSn(OH)_6$ derived from the peptized $SnO_2 \cdot xH_2O$ sol (pH = 9.3) is

constituted of much smaller clusters ranging from 20 to 200 nm (Figure 3b). The clusters connect with each other loosely. The size of their nanocrystallites can be estimated to 3 nm. Obviously peptization is quite helpful to reduce the agglomeration and also to decrease the particle size of the powder.

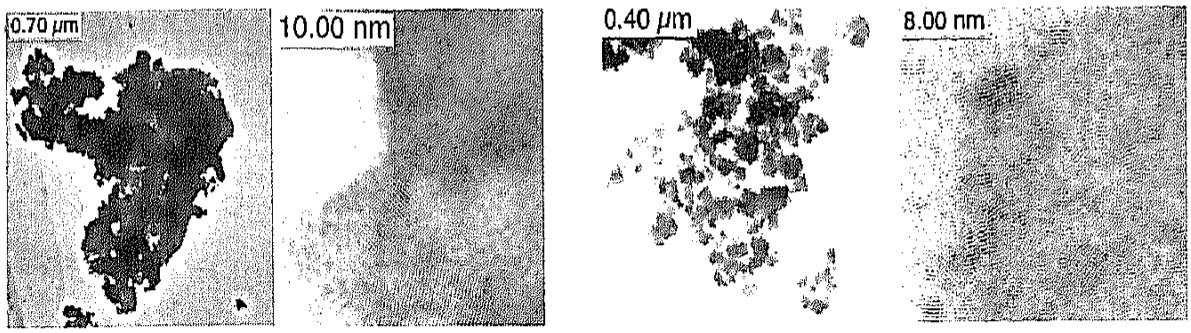



Fig. 3 HR-TEM micrographs of the as-prepared powder of $BaSn(OH)_6$ derived from: (a) the $SnO_2 \cdot xH_2O$ gel, (b) the peptized $SnO_2 \cdot xH_2O$.

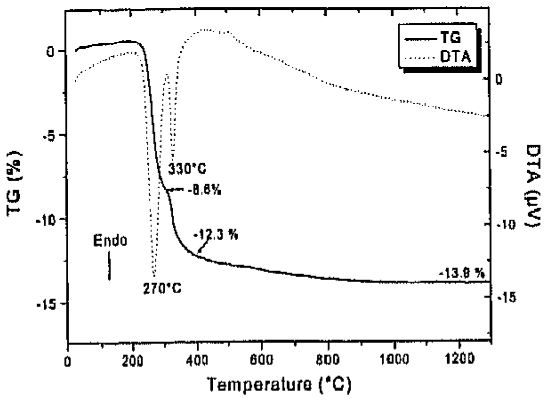



**Fig. 4** TG-DTA curve of the as-prepared powder derived from the peptized precursor. Heating rate is 10°C/min.

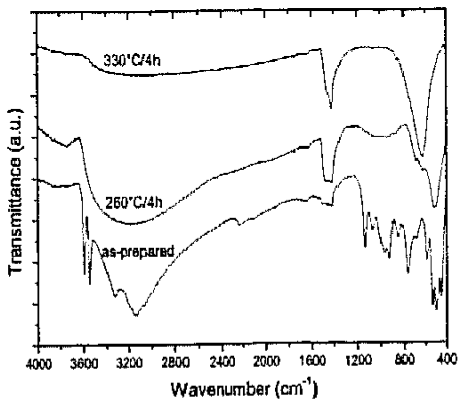



**Fig. 5** FTIR spectra of the powder derived from the peptized precursor calcined at various temperatures for 4 hours.

In figure 4 the TG-DTA-curve shows two endothermic peaks at 270°C and 330°C, corresponding to the dehydration and dehydroxylation process of the as-prepared powder. As a result, most of weight loss occurs between 200 to 400°C.

In FTIR diagram (Fig. 5) the Sn-OH group (five-set peaks around 500 $cm^{-1}$) in the powder disappears at 330°C. The octahedron structure [$SnO_6$] (630 $cm^{-1}$) appears at 260°C. Thus, the structure rearrangement begins at 260°C and finishes at 330°C.

The powder consists of $BaSn(OH)_6$, which was confirmed by XRD (Fig. 6). It transforms into an amorphous phase after being calcined at 260°C for 4 hours. $BaSnO_3$ nucleates from the amorphous phase and grows either by increasing the temperature or extending the treatment time. A single-phase $BaSnO_3$ nanopowder with a crystallite size of 27.6 nm (determined by XRD) was obtained at 330°C after 4h of calcination. The BET specific surface area of this powder is 23.5 $m^2/g$, while that from the non peptized $SnO_2 \cdot xH_2O$ gel is only 5.3 $m^2/g$.

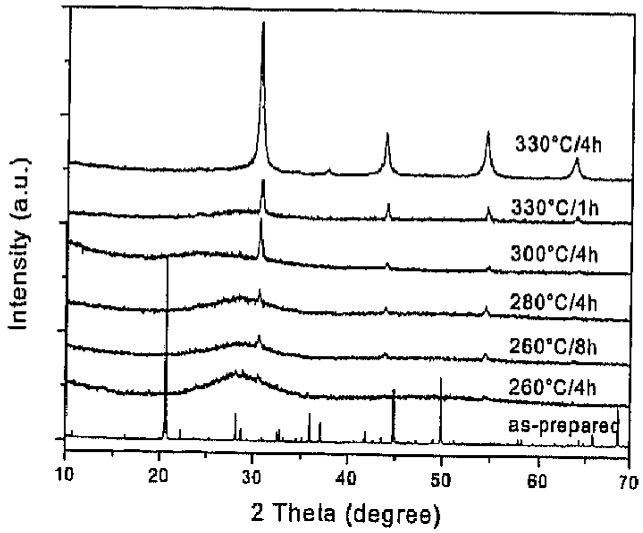



Fig. 6 XRD patterns of the as-prepared powder derived from the peptized precursor calcined at various temperatures and times.

## 4. Summary

A single-phase nanocrystalline $BaSnO_3$ powder with a specific surface area of 23.5 $m^2/g$ has been obtained utilizing a peptized tin oxide hydrate precursor instead of a gel. The agglomeration and particle size of the hydrothermal formed $BaSn(OH)_6$ was reduced due to this peptization. $BaSn(OH)_6$ transforms during calcination over an amorphous phase into nanoscaled $BaSnO_3$.

## References

[1] U. Lumpe, J. Gerblinger and H.Meixner, Sensors and Actuators B, 24-25(1995)657-660.

[2] H. Sano, R. H. Herber, Moessbauer parameters of barium stannate, J. Inorg. Nucl. Chem. 30(1968)2, 409-413.

[3] T.R.N. Kutty and R. Vivekanadan, Mat. Res. Bull., 22(1987)11, 1457-1465.