Hydrothermal synthesis of nanocrystalline BaSnO₃ using a SnO₂·xH₂O sol

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Abstract

A BaSnO₃ powder with a crystallite size of 27.6 nm has been prepared through a hydrothermal reaction of a peptised SnO₂·xH₂O and Ba(OH)₂ at 250 °C and the following crystallization of this hydrothermal product at 330 °C. The peptisation of the SnO₂·xH₂O gel is dependent on the pH value. Through peptisation the mean particle size of SnO₂·xH₂O in the aqueous solution has been decreased by a factor of 100 to 8 nm. A limited agglomeration in the sol-prepared powder has been observed under the microscope. The structure evolution and crystallisation behaviours of the sol-prepared powders were investigated by TG-DTA, IR and XRD. The BaSn(OH)₆ phase in the as-prepared powder transforms into an amorphous phase at 260 °C, from which the BaSnO₃ particles nucleate and grow with an increase in temperature. The single-phase BaSnO₃ powder has been obtained at a temperature as low as 330 °C. This sol-prepared powder is more sinter-reactive than the gel-prepared powder and can be sintered to a ceramic with 90.7% of the theoretic density.

Keywords: Powders-chemical; Preparation; Electron microscopy; X-ray methods; Perovskites; Sensors; BaSnO₃

1. Introduction

As a perovskite-structured ceramic BaSnO₃ is becoming more and more important in material technology because of its characteristic dielectric properties. It has been used to prepare thermally stable capacitors¹,² and to fabricate ceramic boundary layer capacitors when combined with BaTiO₃.³,⁴ In recent years BaSnO₃ has been found to be a very promising sensor material and therefore received much attention. In pure as well as doped forms stannates have been employed as sensor materials for a lot of gases, including CO, H₂, Cl₂, NOₓ and humidity.⁵–⁹ BaSnO₃ has also been used in the preparation of multifunctional temperature–humidity–gas sensors in combining with BaTiO₃.¹⁰

The BaSnO₃ powder is conventionally prepared by ceramic solid reaction through sintering BaCO₃ and SnO₂ at a high temperature ranging from 1200 to 1400 °C.¹¹,¹² A preparation of the BaSnO₃ powder by heating a coprecipitate of hydrated barium stannates at 1000 °C was reported by Coffen.¹³ However, the often simultaneously formed solid barium tin hydroxide made it difficult to obtain the phase-pure BaSnO₃ at high temperatures.¹⁴ A modified sol–gel method¹⁵ was used to prepare BaSnO₃ powder from tin chloride and barium carbonate by adding a chelating agent such as citric acid, the synthesised aqueous gel had nevertheless to be calcined at 600 °C for 5 h and than annealed at 1000 °C for 17 h to convert into a BaSnO₃ powder. Azad and Hoss⁶ tried to prepare BaSnO₃ by the self-heat-sustained route from metallic tin powder and anhydrous Ba(NO₃)₂. However, a high calcination temperature more than 1200 °C is necessary to obtain phase-pure BaSnO₃. A polymerised complex method¹⁶ was also taken to prepare BaSnO₃ powder, in which a barium tin citric acid complex precursor was converted into aggregated BaSnO₃ by treating at a temperature range of 600–900 °C, but it is difficult to remove the trace amounts of BaCO₃ and SnO₂ even at 900 °C.

Compared with the above described synthesis methods, the hydrothermal synthesis route reported by Kutty and Vivekanandan¹⁷ for preparing BaSnO₃ powders shows its advantage in the low synthesis temperature. Fine BaSnO₃ powders can be prepared by this method starting from a SnO₂·xH₂O gel at a temperature as low as 260 °C. However, the particle size of the obtained powder is in the micrometer
region (0.2–0.6 μm). A low specific surface area resulting from such large particles (the specific surface area which was not referred in the literature 18 could be estimated to be 1.38–4.14 m²/g according to the particle size without consideration of the aggregation) is not beneficial to the sensitivity of the sensing device. It is known that the detection of gas in the sensors containing BaSnO₃ is performed by measurement of the changes in electrical properties such as conductivity. The changes are induced in the semiconducting BaSnO₃ following the adsorption of some gases on the solid surface. The mechanism of the gas sensitivity of this semiconductor oxide is a surface reaction process.8,9 Thus a large surface area of the oxide powder is of importance to its characteristic sensor properties. For obtaining a large surface area the main task is to decrease the degree of aggregation between the particles. As well as SnO₂·H₂O as is concerned, its agglomerates can be redispersed into a colloidal solution through peptisation10 (the process of converting a gel to a sol). Thus, the aim of this paper is to prepare a perovskite BaSnO₃ powder with a large specific surface area through peptisation of the SnO₂·H₂O gel. The thermal behaviours, the structure evolution, the crystallisation behaviours and the sintering properties of the obtained stannate powder are also reported here.

2. Experimental procedure

The precursor SnO₂·H₂O gel was synthesised according to the literature20 by adding 2.5 M ammonia solution to 1 M SnCl₃ solution at an ice bath. To remove the Cl⁻ ions the gel was washed with distilled water several times until its electric conductivity was less than 50 μS/cm. For obtaining a sol the washed gel was diluted to 0.3 M, in which 25% ammonia solution as a peptisator was added slowly under stirring. The amount of the ammonia solution was controlled by measuring the pH value of the mixture. The tin oxide hydrate sol was then mixed with 0.2 M Ba(OH)₂ solution by stirring. The amount of the ammonia solution was controlled as the pH-value exceeds 8.3. In the experiments the pH-value was controlled at pH 9.3 by adding the ammonia solution as a peptisator was freshly synthesised because an aged gel will lose its activity through losing the hydrated water.22 For example, a aged gel (three days) could not be peptised. Thus a large surface area of the oxide powder is of importance to its characteristic sensor properties. For obtaining a large surface area the main task is to decrease the degree of aggregation between the particles. As well as SnO₂·H₂O as is concerned, its agglomerates can be redispersed into a colloidal solution through peptisation (the process of converting a gel to a sol). Thus, the aim of this paper is to prepare a perovskite BaSnO₃ powder with a large specific surface area through peptisation of the SnO₂·H₂O gel. The thermal behaviours, the structure evolution, the crystallisation behaviours and the sintering properties of the obtained stannate powder are also reported here.

3. Results and discussion

The SnO₂·H₂O gel suspended in water can be peptised by using ammonia solution as the peptising agent. It was found that the peptising effect of ammonia to the SnO₂·H₂O gel depends on the pH value. The suspensions with a pH from 6.8 to 7.2 are milky white, which cannot change into transparent sols even after being aged for a long time. At a pH value between 8.3 and 9.8 the suspensions convert into transparent sols through peptisation within 2–12 h. The higher the pH value, the less time is necessary for the peptisation. The particle diameter distribution of the samples at different pH values are shown in Fig. 1. It can be seen from Fig. 1a that the particle diameter of samples at pH 6.8 and pH 7.2 distributes in a range from 0.5 to 1.5 μm while at pH 8.3 to pH 9.8 in a range less than 20 nm. Fig. 1b shows the dependence of the mean particle diameter (d₅₀-value of the volume distribution) of the samples on the pH-value. A sharp decrease of the d₅₀-value can be observed at pH between 7.2 and 8.2, where the d₅₀ is decreased from about 0.8 μm by a factor of 100 to 8 nm.

From this it can be concluded that a tin oxide hydrate sol will be formed from the tin oxide hydrate gel through peptisation as the pH-value exceeds 8.3. In the experiments the pH value was controlled at pH 9.3 by adding the ammonia solution for obtaining a stable SnO₂·H₂O sol within 6 h. It should be pointed out that the SnO₂·H₂O gels used for peptisation was freshly synthesised because an aged gel will lose its activity through losing the hydrated water.23 For example, a aged gel (three days) could not be peptised.

The powders synthesised from the SnO₂·H₂O gel or the SnO₂·H₂O gel by hydrothermal reaction with the Ba(OH)₂ solution at 250°C for 6h consist of BaSn(OH)₆ (this will
Fig. 1. (a) Particle diameter contribution, (b) mean particle diameter $d_{50}$ of the tin oxide hydrate peptised at different pH.

be discussed later). Figs. 2 and 3 show the HR-TEM micrographs of the powders derived from the SnO$_2$·$x$H$_2$O gel and the SnO$_2$·$x$H$_2$O sol, respectively (the marked particles are processed with Fourier-transformation, Fourier-filtering and morphologic operation). Fig. 2a indicates the high agglomeration state of BaSn(OH)$_6$, not even a single particle is recognisable. Fig. 2b shows that these agglomerates consist of many overlapped crystallites with a diameter of 10–50 nm. In contrast to this, BaSn(OH)$_6$ derived from the SnO$_2$·$x$H$_2$O sol is constituted of much smaller clusters ranging from 20 to 200 nm (Fig. 3a). The clusters connect with each other loosely. It is shown from the structure image (Fig. 3b) that the size of the nanocrystallites is about 3 nm. Therefore, peptisation is helpful to minimise the agglomeration of the particles and lower the particle size of the powders.

Fig. 4 shows the TG-DTA curve of the powders prepared from the sol. Two endothermic peaks located at 270 and 330 $^\circ$C can be found in the DTA curve, which corresponds to the dehydration and dehydroxylation process of the sol-prepared powder. In accordance with the DTA curve, two main weight loss stages, namely from room temperature to 300 $^\circ$C and from 300 to 400 $^\circ$C, can be found in

![Image](https://via.placeholder.com/150)
Fig. 3. HR-TEM micrographs of the sol-prepared powder of BaSn(OH)\(_6\): (a) diffraction contrast imaging, (b) structure imaging. BaSn(OH)\(_6\) was hydrothermally synthesised from the SnO\(_2\)·xH\(_2\)O sol and Ba(OH)\(_2\) at 250\(^\circ\)C for 6 h.

The TG curve. The weight loss in the first stage and the second stage is 8.6 and 3.7 wt.\%, respectively. Thereafter the weight decreases slowly from 400 to 800 \(^\circ\)C (1.6 wt.\%). Above 800 \(^\circ\)C little weight change can be observed. Calculated from the TG results, the constitution of the as-prepared powder can be noted as BaSnO\(_3\)·2.73H\(_2\)O, it becomes BaSnO\(_3\)·1.04H\(_2\)O and BaSnO\(_3\)·0.31H\(_2\)O at 300 and 400 \(^\circ\)C, respectively.

To study the crystallisation behaviour of the sol-prepared powder, the powder was calcined at different temperatures ranging from 260 to 330 \(^\circ\)C for definite time. Fig. 6 shows the XRD patterns of these samples. The as-prepared powder consists of BaSn(OH)\(_6\). It transforms into amorphous after being calcined at 260 \(^\circ\)C for 4h. BaSnO\(_3\) nucleates from the amorphous phase and grows either by increasing the temperature or extending the treatment time, the effect of the temperature is nevertheless more obvious. The transformation of BaSn(OH)\(_3\) to BaSnO\(_3\) ends at 330 \(^\circ\)C and a single-phase BaSnO\(_3\) powder was obtained at 330 \(^\circ\)C after 4h of calcination. The crystallite size of the BaSnO\(_3\) calculated according to Scherrer equation is 27.6 nm.

By comparison, the crystallisation process of the gel-prepared powder was investigated with XRD and the results are illustrated in Fig. 7. The as-prepared powder also consists of BaSn(OH)\(_3\). It transforms into amorphous after calcining at 260 \(^\circ\)C for 0.25h. By extending the time to 1h, a BaSnO\(_3\) phase appears. The conversion of the amorphous phase into perovskite-type BaSnO\(_3\) accomplishes after 4h of calcination at 260 \(^\circ\)C. Thus, the single-phase BaSnO\(_3\) can be prepared at 260 \(^\circ\)C from the gel-prepared powder. However, even at a lower calcining temperature of 260 \(^\circ\)C (4h) the crystallite size of the gel-prepared BaSnO\(_3\) is 33.0 nm and larger than that of the BaSnO\(_3\) powder obtained by calcining the sol-prepared BaSn(OH)\(_3\) at 330 \(^\circ\)C for 4h.

The BET specific surface area of the BaSnO\(_3\) powder by calcining the sol-prepared BaSn(OH)\(_3\) at 330 \(^\circ\)C for 4h is 23.5 m\(^2\)/g while that from the gel-prepared powder at 260 \(^\circ\)C/4h is only 5.3 m\(^2\)/g. The obvious increase in specific surface area through peptising the gel can be attributed to the reduction in aggregation between the particles and the decrease in particle size of SnO\(_2\)·xH\(_2\)O.

The shrinkage behaviour of sol- and gel-prepared BaSnO\(_3\) was studied by means of dilatometry. The green densities of uniaxially pressed sol- and gel-prepared samples (400 MPa) are 47.8 and 45.0\% of the theoretic density of BaSnO\(_3\) (7.24 g/cm\(^3\)), respectively. Fig. 8 shows their shrinkage curves.
Fig. 4. TG-DTA curve of the sol-prepared powder of BaSn(OH)$_6$. The powder was hydrothermally synthesised from the SnO$_2$·xH$_2$O sol and Ba(OH)$_2$ at 250°C for 6 h. The heating rate is 10°C/min.

Fig. 5. FTIR spectra of the sol-prepared powder calcined at various temperatures for 4 h. The powder was hydrothermally synthesised from the SnO$_2$·xH$_2$O sol and Ba(OH)$_2$ at 250°C for 6 h.

Fig. 6. XRD patterns of the sol-prepared powder calcined at various temperatures and times. The as-prepared powder was hydrothermally synthesised from the SnO$_2$·xH$_2$O sol and Ba(OH)$_2$ at 250°C for 6 h.

Fig. 7. XRD patterns of the gel-prepared powder calcined at 260°C for different time. The as-prepared powder was hydrothermally synthesised from the SnO$_2$·H$_2$O gel and Ba(OH)$_2$ at 250°C for 6 h.

Fig. 8. Dilatometry curves of BaSnO$_3$ (BSO) obtained by calcining the gel-prepared BaSn(OH)$_6$ powder at 260°C for 4 h and that obtained by calcining the sol-prepared BaSn(OH)$_6$ at 330°C for 4 h. Heating rate: 10°C/min.
sintering begins at 1450°C and a shrinkage of only 10.2% is reached at 1650°C. The upper limit of the temperature of equipment is 1650°C where the sintering process of the sol-prepared sample is not ended. In contrast to that, the onset of the sintering temperature of the sample derived from the sol is lowered to 1200°C and its shrinkage reaches 17.9% at 1650°C. Judging from the flattening of the curve near 1650°C, it can be said that the sintering process of this sample is almost complete. It therefore can be concluded that the sample derived from the sol is more sinter-active.

The increase of the sinter-activity can be attributed to smaller particles and the larger surface area which is the driving force of the sintering process.

BaSnO₃ pellets formed under a cold isostatic pressure of 400 MPa were sintered at the same temperature of 1600 °C for 4 h for comparison. Using the gel-prepared powder a bulk density of 5.47 g/cm³ (75.6% of the theoretic density) resulted while using the sol-prepared powder a bulk density of 6.57 g/cm³ (90.7% of the theoretic density) could be obtained. Fig. 9a and b shows the microstructure of the polished surface of two samples sintered at 1600 °C for 4 h, starting from the gel- and sol-prepared BaSnO₃ powders, respectively. For the gel-prepared sample (Fig. 9a), the powder did not densified enough so that the pores still connect with each other. In contrast to this, the sol-prepared ceramic (Fig. 9b) are much more dense and only some isolated pores can be observed. At a sintering temperature of 1600 °C, the grain size of both samples is in the μm-region. Generally the grains of the sol-prepared sample are finer than those of the gel-prepared sample, but some grains as large as 2–3 μm in the former can also be observed. The large grain size in the BaSnO₃ ceramic can be attributed to the grain growth at the high sintering temperature.

4. Summary

In this study, a single-phase nano-crystalline BaSnO₃ powder with a specific surface area as large as 23.5 m²/g has been prepared through the hydrothermal reaction between tin oxide hydrate sol and Ba(OH)₂ at 260 °C and the following crystallisation of the resulted powder at 330 °C. The tin oxide hydrate sol was obtained by peptising the tin oxide hydrate gel through adding the ammonia solution. The peptisation is dependent on the pH value and the particle sizes of the tin oxide hydrate sol are in the range less than 20 nm. Through peptisation the agglomeration and aggre-
gation between the particles in the sol-prepared powder is limited and the crystallite size is decreased from 10–50 nm to about 3 nm. As a result, the BaSnO₃ powder obtained at 330 °C shows a much larger specific surface area. During the thermal treatment of the sol-prepared powder, the dehy-
droxylation and dehydration of BaSn(OH)₆ begins at 260 °C and ends at 330 °C. As a result of the structure rearrange-
ment at 260 °C, the BaSn(OH)₆ phase transforms into an amorphous phase, from which the BaSnO₃ phase nucleates and grows with an increase in temperature. This transfor-
mation is finished at 330 °C. The sol-prepared powder is more sinter-active than the gel-prepared one. A BaSnO₃ ceramic with a 90.7% theoretic density has been obtained by sintering the sol-prepared powder at 1600 °C for 4 h.

References


