J Mater Sci (2007) 42:10007–10013
DOI 10.1007/s10853-007-2069-9

Preparation and characterization of $BaSnO_3$ powders by hydrothermal synthesis from tin oxide hydrate gel

Wensheng Lu · Helmut Schmidt

Received: 10 November 2006 / Accepted: 27 July 2007 / Published online: 6 September 2007

Abstract $BaSnO_3$ powders have been prepared from the tin oxide hydrate gel and the $Ba(OH)_2$ solution via hydrothermal synthesis route. The influence of the process parameters on the characteristics of $BaSnO_3$ has been studied. A powder with the single-phase of $BaSnO_3$ can be obtained only when the concentration of $Ba(OH)_2$ solution is no less than 0.2 M and the ratio of Ba:Sn lies between 1.0 and 1.2. At a hydrothermal temperature of 330 °C or higher, uniform $BaSnO_3$ powders can be directly prepared through hydrothermal reaction. When the hydrothermal temperature is lower than 250 °C, the as-prepared powder consists of $BaSn(OH)_6$ that transforms through an amorphous phase into $BaSnO_3$ by calcination at 260 °C. In the hydrothermal temperature range of 130–250 °C, a higher temperature can promote the crystallization of $BaSnO_3$, increases its specific surface area and decreases the average particle size. The duration of the hydrothermal reaction affects the morphology of the powder particles. The effects of the nonaqueous solvents on the properties of powders have also been investigated.

Introduction

Perovskite-type $BaSnO_3$ has been used to prepare capacitors because of its characteristic dielectric properties [1–4]. In recent years, $BaSnO_3$ has received more attention for its application as a sensor material for a lot of gases, including CO, Cl_2, NO_x, O_2, CO_2, C_2H_5OH, CH_3SH, humidity and liquefied petroleum gas [5–14].

The $BaSnO_3$ powder is conventionally prepared by solid reaction through sintering $BaCO_3$ and SnO_2 at a high temperature ranging from 1,200 °C to 1,400 °C [15, 16]. A hydrothermal synthesis route for the preparation of $BaSnO_3$ was first reported by Kutty and Vivekanadan [17]. Starting from a tin oxide hydrate gel ($SnO_2{\cdot}xH_2O$), fine $BaSnO_3$ powders can be prepared at a temperature as low as 260 °C. Another advantage of this route offered is the high purity of the prepared powders. Udawatte and Yoshimura [18] prepared the single-phase $BaSnO_3$ powder from the hydrothermal reaction of the dried tin oxide hydrate gel and $Ba(OH)_2$ at 300 °C. Jaeger et al. [19] prepared rod-like $BaSn(OH)_6$ through hydrothermal treatment of the tin oxide hydrate gel and $Ba(OH)_2$ solution at 180 °C. Using this method we obtained nanocrystalline $BaSnO_3$ powder from the tin oxide hydrate sol and $Ba(OH)_2$ solution at 330 °C [20]. However, a detailed investigation of the influence of the processing parameters of the hydrothermal synthesis on the properties of the $BaSnO_3$ has not been reported up to date. The processing parameters nevertheless affected the properties of other synthesized ceramic powders such as $BaTiO_3$ [21, 22] and $PbTiO_3$ [23, 24] strongly. It has been found [23, 25–27] that the starting materials ratio and their concentrations can influence the composition, the morphology, and the particle size as well as the aggregation degree of the resulted powders. Nonaqueous solvents [28, 29] were also employed during

W. Lu (✉)
Leibniz-Institut fuer Neue Materialien gGmbH, Im Stadtwald, Gebaeude D2 2, 66123 Saarbruecken, Germany
e-mail: lu.wensheng@gmail.com

H. Schmidt
Universitaet des Saarlandes, Lehrstuhl fuer Neue Materialien, Beethovenstraße Zeile 4, 66125 Saarbruecken-Dudweiler, Germany
e-mail: h.schmidt@nm.uni-saarland.de

hydrothermal reaction (also called lyothermal synthesis) to tailor the properties of the resulted powders.

It will be not overstated that the temperature is the most important parameter during the hydrothermal reaction, because the main properties of the products are dependent on this parameter [23, 30–32]. The importance of the hydrothermal temperature for preparing $BaSnO_3$ is nevertheless not revealed enough in the literature [17–20]. Therefore, the aim of the presented article is to investigate the effects of some important parameters, especially the temperature, on the properties of the resulted $BaSnO_3$ powder.

Materials and methods

Chemicals

Ammonia solution (25 wt.%) was purchased from SDS. Tin tetrachloride pentahydrate (98 wt.%) was purchased from Aldrich. Barium hydroxide octahydrate (98 wt.%), methanol (99.8 wt.%), isopropanol (99.5 wt.%) were obtained from Fluka. Ethanol (99.5 wt.%) was obtained from Riedel de Haen.

Hydrothermal synthesis

The precursor $SnO_2 \cdot xH_2O$ gel was synthesized by adding 160 mL 2.5 M ammonia solution to 120 mL 1 M $SnCl_4$ solution in an ice bath under stirring for 1 h. To remove the Cl^- ions the gel was washed with distilled water several times until its electric conductivity was less than 50 µS/cm. The tin oxide hydrate gel was then suspended in $Ba(OH)_2$ solution by using argon as the protecting gas. The suspension was thereafter charged in a 250 mL teflon-lined autoclave (DAH 904, Berghof) or a 250 mL steel autoclave (Medimex), depending on the hydrothermal temperature, and treated at hydrothermal temperatures ranging from 130 °C to 350 °C under the autogenous pressure for 0.5–10 h. The educt was taken out at room temperature and washed with distilled water until its pH value was near 7. The powders were then dried in a vacuum furnace at 60 °C for 2 days (noted as as-prepared powder). Some samples were further calcined in an oven for crystallization at 260 °C for 4 h (also called as end-powder).

Characterization

The crystalline phase of the powder was analyzed with a D500 model diffractometer (Simens, radiation CuKα1) operating at 40 kV. The crystallite size was calculated from Scherrer equation [33]. The infrared spectra of the samples were recorded with a Fourier transform infrared spectrometer (IFS 25v, Bruker). The morphology of powders were observed under a scanning electron microscope (SEM: JSM 6400F, JEOL). For a quantitative element analysis, energy dispersive X-ray spectrometry (EDX: Noran Instruments) was applied. The specific surface area of the powders were characterized with a BET gas adsorption analyzer (ASAP 2400, Micrometrics). The density of the powder was measured with a gas pycnometer (Micrometrics).

Results and discussion

Influence of the $Ba(OH)_2$ concentration

The concentration of the $Ba(OH)_2$ solution was changed from 0.05 M to 0.4 M for studying its influence on the properties of the resulted powders. The $Ba(OH)_2$ solution reacted with the tin oxide hydrate gel with a molar rate of Ba:Sn = 1 at a hydrothermal temperature of 250 °C for 6 h. The educt was thereafter calcined at 260 °C for 4 h to obtain $BaSnO_3$. XRD analysis (Fig. 1a) indicates that an increase in the $Ba(OH)_2$ concentration promotes the crystallization of the as-prepared powder which consists of $BaSn(OH)_6$. By comparison with tin oxide hydrate ($Ba(OH)_2 = 0$), we can see that there are still traces of not-reacted tin oxide hydrate existing in the powder in the cases of 0.05 M and 0.1 M while no impure phase in the cases of 0.2 M and 0.4 M. It is shown in Fig. 1b that the end-powders at 0.2 M and 0.4 M are made up of $BaSnO_3$ while the end-powders at 0.05 M and 0.1 M contain the cassiterite phase besides $BaSnO_3$. The EDS results show that the ratio of Sn to Ba in the calcined powder at 0.05 M is 5.90 while at 0.4 M, 1.02. This agrees well with the XRD analysis and confirms that a very dilute $Ba(OH)_2$ solution is not suitable to prepare the $BaSnO_3$ powder. The formed cassiterite phase can be contributed to the incomplete precipitation of $BaSn(OH)_6$ at lower pH-values of the lower $Ba(OH)_2$ concentration.

We noticed that Buscaglia and his colleagues [34] prepared $BaSn(OH)_6$ from 0.05 M $BaCl_2$-$SnCl_4$ solution at 100 °C by the coprecipitation method. The amount of the NaOH as the precipitating agent used was greatly in excess, which can guarantee the pH value needed für the formation of $BaSn(OH)_6$. In the case of the hydrothermal reaction, $Ba(OH)_2$ acts as the reacting agent and the pH controlling agent. As the concentration of OH^- in the solution is not high enough to provide the necessary pH condition for the precipitation, it is understandable that no $BaSn(OH)_6$ is obtained as described in the literature [35].

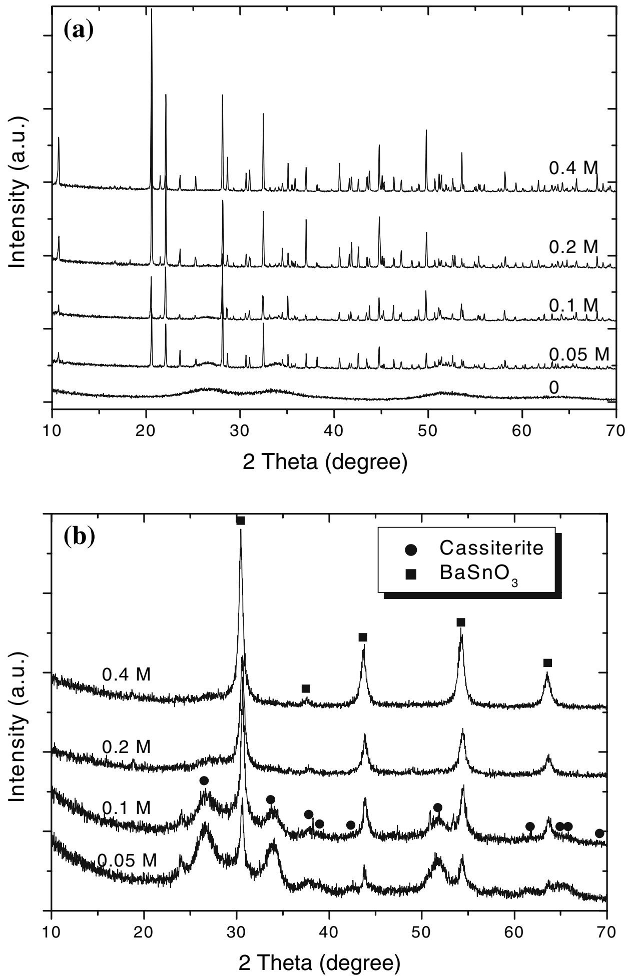

Fig. 1 XRD patterns of (**a**) as-prepared powders, (**b**) powders calcined at 260 °C for 4 h versus the concentration of $Ba(OH)_2$. The as-prepared powder was synthesized hydrothermally at 250 °C for 6 h

The dependence of the specific surface area and the density of the as-prepared powder on the concentration of $Ba(OH)_2$ is shown in Fig. 2. It can be found that the specific surface area and the density decrease with an increase in $Ba(OH)_2$ concentration up to 0.2 M. The reasons are that tin oxide hydrate has a larger specific surface area (190 m^2/g) and a higher density (4.75 g/cm^3) in comparison to $BaSn(OH)_6$, and that some tin oxide hydrate still exists in the as-prepared powder at low concentrations. From 0.2 M to 0.4 M there is little change in density and a small decrease in specific surface area, the average particle size calculated from the specific surface and the density will increase. This suggests that a further increase in $Ba(OH)_2$ concentration will cause an increase in the degree of agglomeration of the particles.

Based on above results and the fact that the saturate solubility of $Ba(OH)_2$ at 20 °C is 0.2 M, the optimal $Ba(OH)_2$ concentration for prpepation of $BaSnO_3$ can be determined as 0.2 M.

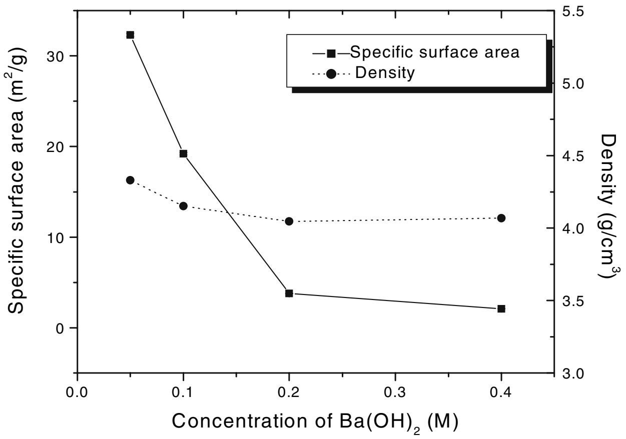

Fig. 2 Specific surface area and density of the as-prepared powder which was synthesized hydrothermally at 250 °C for 6 h as a function of the concentration of $Ba(OH)_2$

Influence of the molar ratio of Ba to Sn

The ratio of Ba to Sn varied from 0.5 to 2. The educts, after being hydrothermally treated at 250 °C for 6 h, were calcined at 260 °C for 4 h to realize the crystallization of $BaSnO_3$. The XRD patterns of the calcined powder are shown in Fig. 3. It indicates that at a low ratio from 0.5 to 0.9, where the content of barium is deficient, cassiterite and $BaSnO_3$ exist simultaneously in the powder. Some unknown phases can also be found when the ratio is 0.8 or 0.9. Apparently cassiterite results from the not reacted tin oxide hydrate. In the ratio range of 1–1.2, the powder is made up of the single-phase $BaSnO_3$. When the Ba:Sn ratio reaches 1.5, some unknown phases appear again and coexist with $BaSnO_3$. No cassiterite can be discerned. At the ratio of Ba:Sn = 2, $BaSnO_3$ coexists with an amorphous phase which can be discerned from the contour of

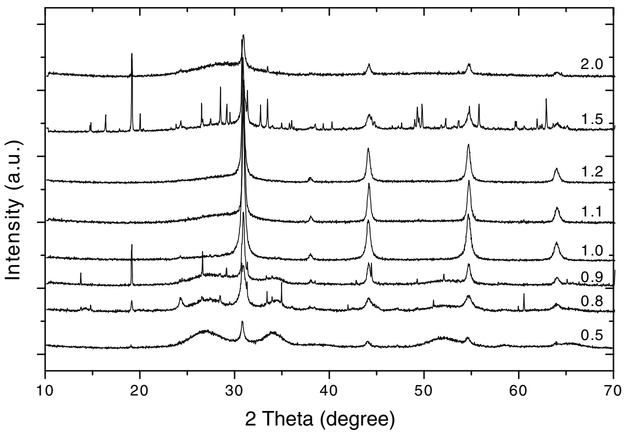

Fig. 3 XRD patterns of powders synthesized hydrothermally at different Ba:Sn ratios at 250 °C for 6 h and then calcined at 260 °C for 4 h

Table 1 Dependence of the properties of the powder hydrothermally prepared at 250 °C for 6 h on the molar ratio of Ba:Sn

Ratio of Ba to Sn	Density (g/cm^3)	Specific surface area (m^2/g)	Crystallite size of $BaSnO_3^*$ (nm)
1.0	4.23	3.42	36
1.1	4.21	2.56	44
1.2	4.13	0.79	46

* calculated from XRD patterns of the powders calcined at 260 °C for 4 h

the curve in the powder. It is also worth noting that the degree of crystallization of the powder is related to the ratio of Ba to Sn. The intensity of the crystalline peaks of $BaSnO_3$ shows clearly that the equivalent addition of Ba and Sn promotes the crystallization of $BaSnO_3$.

Since the single-phase $BaSnO_3$ can only be obtained at a Ba:Sn ratio ranging from 1 to 1.2, it is of interest to study the effects of the Ba:Sn ratio in this range on the properties of the $BaSnO_3$ powder. Table 1 shows that an increase in ratio within this range will lead to a decrease in density, specific surface area and an increase in crystallite size of $BaSnO_3$, though the differences are not large. This means that a lower ratio from 1 to 1.2, namely an equimolar reaction between $Ba(OH)_2$ and $SnO_2{\cdot}xH_2O$, is beneficial to obtain $BaSnO_3$ powder with a better quality.

Hydrothermal temperature and time

The phase transformation as a function of the hydrothermal temperature ranging from 130 °C to 350 °C was examined. The XRD patterns of the educts obtained at different temperatures are illustrated in Fig. 4. Synthesized at a temperature between 130 °C and 250 °C, the hydrothermal product mainly consists of $BaSn(OH)_6$. When the temperature is increased to 300 °C, although the product consists mainly of $BaSn(OH)_6$, a trace of $BaSnO_3$ can be found in it. Above 330 °C, $BaSnO_3$ becomes the dominant phase in the powder. The results indicate that a $BaSnO_3$ powder can be directly synthesized via the hydrothermal reaction when the temperature is high enough. The coexistence of $BaSnO_3$ and $BaSn(OH)_6$ at 300 °C suggests $BaSnO_3$ can be formed either directly nucleate from the synthesis solution or directly from the transformation of $BaSn(OH)_6$. This differs from the phase transformation by calcination, where $BaSn(OH)_6$ converts through an amorphous phase into $BaSnO_3$, which will be discussed later. The SEM micrographs of the $BaSnO_3$ powder prepared at 330 °C are shown in Fig. 5. The particles with a dimension of 3–4 µm show a cubic morphology and are very uniform. The specific surface area of the obtained powder is 0.68 m^2/g. Compared with the powder prepared by Udawatte and Yoshimura [18], where the dried tin oxide hydrate gel was used, the size of our powder is smaller and has a more uniform contribution despite the higher hydrothermal temperature. This can be contributed to the decrease in activity and increase in agglomeration of the tin oxide hydrate gel as it is dried. Using the tin oxide hydrate sol as

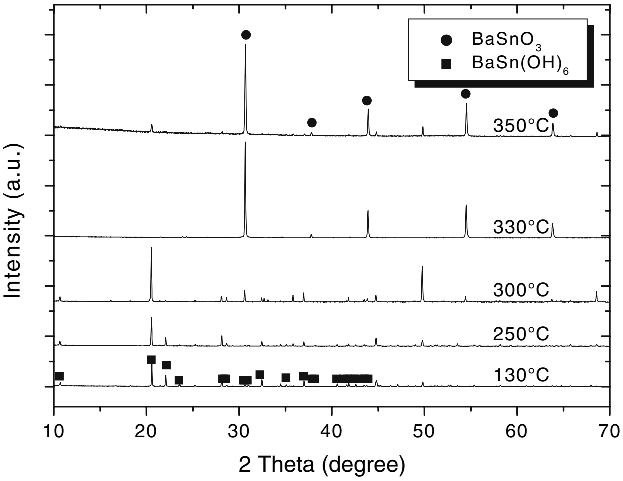

Fig. 4 XRD patterns of the powder synthesized with 0.2 M $Ba(OH)_2$ at different hydrothermal temperatures for 6 h

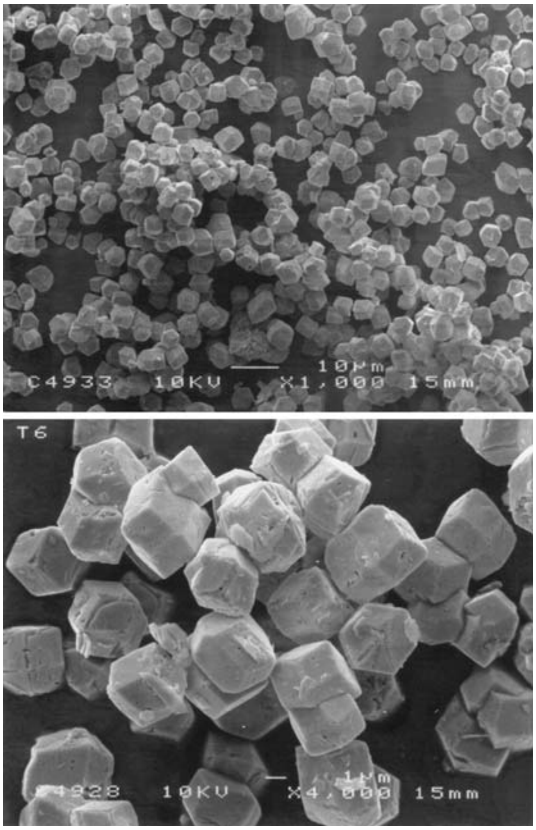

Fig. 5 SEM images of $BaSnO_3$ synthesized at a hydrothermal temperature of 330 °C for 6 h

the starting material, we also obtained a single-phase $BaSnO_3$ at a hydrothermal temperature as low as 280 °C.

A further investigation on the influece of the hydrothermal temperature was carried out in the lower temperature range (≤250 °C), where a Teflon autoclave can be used.

The as-prepared powder synthesized in the lower temperature range consists of $BaSn(OH)_6$. The XRD patterns and the IR spectra of the powders calcined at 260 °C for 4 h are shown in Fig. 6. It can be seen from XRD patterns (Fig. 6a) that the intensity of crystalline peaks of $BaSnO_3$ increases with an increase in hydrothermal temperature. This suggests that a higher temperature promotes the crystallization of $BaSnO_3$, which can also be reflected from the IR spectra (Fig. 6b). With an increase in hydrothermal temperature, the area of the $[SnO_6]$ band centered at 630 cm^{-1} increases.

The effects of the hydrothermal temperature on the specific surface area and the average particle size of the powders (d: nm) which is calculated from the specific surface area (S: m^2/g) and density (D: g/cm^3) according to $d = 6{,}000/(S*D)$ are illustrated in Fig. 7. It can be found that the specific surface area of the as-prepared powder increases with an increase in temperature up to 210 °C, and then becomes constant. Likewise, the average particle size decreases with increasing temperature up to 210 °C and then becomes constant. As for the calcined powder, the specific surface area increases while the average particle size decreases with an increase in hydrothermal temperature up to 250 °C. The calcined powders show a further change from 210 °C to 250 °C in specific surface area and average particle size, compared to the as-prepared powders. This is thought due to the promotion of the crystallization of $BaSnO_3$ at a higher hydrothermal temperature as shown in Fig. 6a.

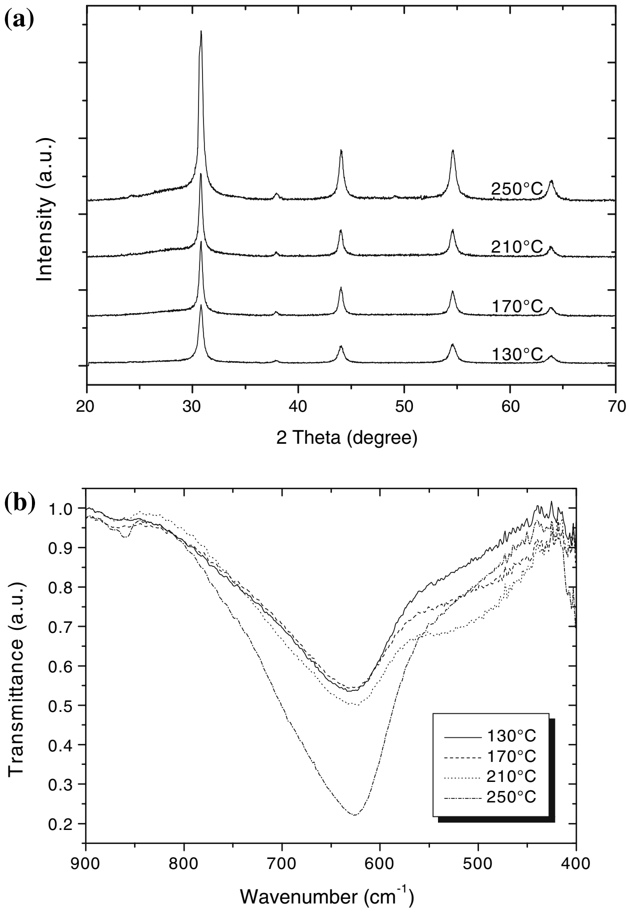

Fig. 6 (**a**) XRD patterns, (**b**) IR spectra of the powders prepared at different hydrothermal temperatures, which were then calcined at 260 °C for 4 h

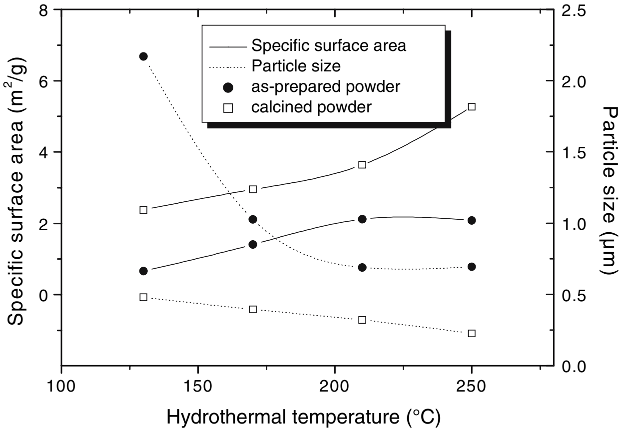

Fig. 7 Specific surface area and the particle size of the as-prepared powders and the corresponding powders calcined at 260 °C for 4 h versus hydrothermal temperature. The particle size is calculated from the specific surface area

Thus, a higher hydrothermal temperature in the range of 130 °C to 250 °C can promote the crystallization of $BaSnO_3$, increase its specific surface area and decrease the average particle size.

The duration of the hydrothermal reaction were changed from 0.5 h to 10 h. The factor time has little effect on the composition and the crystallite size of the powder products. A $BaSnO_3$ powder was obtained through calcination even as the duration of the hydrothermal reaction at 250 °C is only 0.5 h. The crystallite size of $BaSnO_3$ is 35 nm at 0.5 h and changes little with the increase in time. Observed under SEM, the particles of the as-prepared powder change the morphology with the reaction time (Fig. 8). As the time is increased up to 6 h, the particles change from irregular clumps into small smooth and uniform rods. $BaSn(OH)_6$ precipitated from $BaCl_2$-$SnCl_4$ at 100 °C by Buscalia [34] also show the similar rod-like form, but crystallites are agglomerated with each other.

Effects of the solvent

In the case of replacing the aqueous medium by alcohol, the fresh tin oxide hydrate gel precipitated from $SnCl_4$

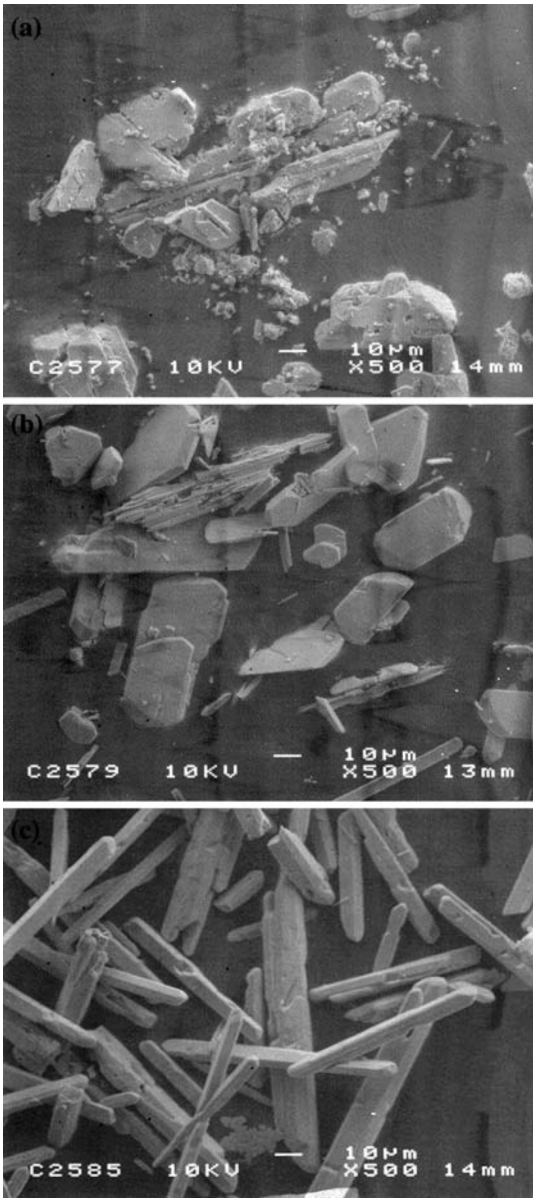

Fig. 8 SEM micrographs of the as-prepared powder synthesized under hydrothermal conditions at 250 °C for different time: (**a**) 0.5 h, (**b**) 2 h, (**c**) 6 h

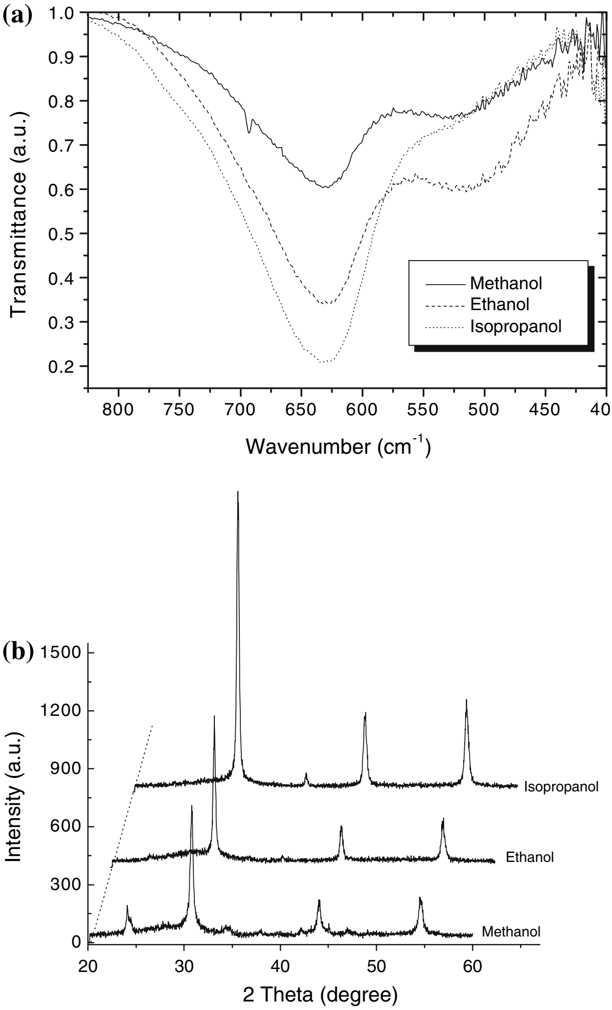

Fig. 9 Dependence of (**a**) IR spectra, (**b**) XRD patterns of the powder hydrothermal prepared at 250 °C for 6 h and then calcined at 260 °C for 4 h on nonaqueous solvents

solution with ammonia solution was suspended in methanol, in ethanol as well as in isopropanol, and then mixed with $Ba(OH)_2 \cdot 8H_2O$ for hydrothermal synthesis. The IR spectra and XRD patterns of the as-prepared powders synthesized at 250 °C for 6 h and then calcined at 260 °C for 4 h are shown in Fig. 9. Figure 9a shows that the $[SnO_6]$ band centered at 630 cm^{-1} intensifies with an increase in carbon atoms. The existence of the band of Sn-OH group around 500 cm^{-1} in the case of methanol and ethanol indicates an incomplete conversion of $BaSn(OH)_6$ into $BaSnO_3$ at 260 °C in the corresponding powders. XRD patterns (Fig. 9b) show that powders synthesized in methanol and ethanol contain impure phases besides $BaSnO_3$ while in isopropanol only $BaSnO_3$ is detected. In addition, isopropanol can be found to promote the crystallization of $BaSnO_3$ according to the intensity of the crystalline peaks. It can therefore be concluded that isopropanol is more suitable for preparing $BaSnO_3$ powder than methanol and ethanol. However, the specific surface area of $BaSnO_3$ prepared in isopropanol (1.74 m^2/g) is smaller than that in water (5.27 m^2/g). The crystallite size of $BaSnO_3$ prepared in isopropanol is 41.3 nm while in water about 35 nm. This result is contrary to that in the $SrTiO_3$ system [28], where alcoholic medium can lead to a decrease in crystallite size.

The crystallization behavior of the sample synthesized at 250 °C for 6 h in water were investigated with XRD and the results are illustrated in Fig. 10. The as-prepared powder consists of $BaSn(OH)_6$. It transforms into amorphous after calcining at 260 °C for 0.25 h. By extending the time to 1 h, a $BaSnO_3$ phase appears. The conversion of

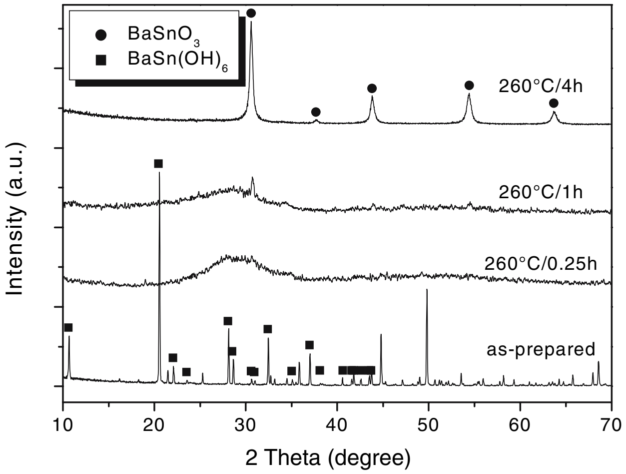

Fig. 10 XRD patterns of the as-prepared powder synthesized at 250 °C for 6 h and calcined at 260 °C for different time

the amorphous phase into perovskite $BaSnO_3$ accomplishes after 4 h of calcination at 260 °C. The results reveal that $BaSn(OH)_6$ is a meta-stable phase which does not directly transform into $BaSnO_3$ but into an amorphous phase. The $BaSnO_3$ nuclei form in the amorphous phase and then grow. This crystallization behavior is the same as $BaSn(OH)_6$ prepared from tin oxide hydrate sol [20].

Summary

$BaSnO_3$ powders have been prepared either directly through hydrothermal synthesis or through hydrothermal reaction in combination with the following calcination. The parameters including $Ba(OH)_2$ concentration, ratio of Ba to Sn, hydrothermal temperature and time as well as solvents play an important role on the properties of the obtained powders. The optimal $Ba(OH)_2$ concentration for preparing $BaSnO_3$ powder is 0.2 M. A single-phase $BaSnO_3$ powder can only be obtained when the ratio of Ba to Sn is between 1.0 and 1.2. An equivalent reaction of Ba and Sn is beneficial to prepare high quality $BaSnO_3$ powders. As the hydrothermal temperature is not less than 330 °C, $BaSnO_3$ can be directly hydrothermally synthesized. In the lower hydrothermal temperature range (130–250 °C), an increase in temperature promotes the crystallization of $BaSnO_3$, increase the specific surface area and decrease the particle size. The duration of hydrothermal reaction affects the morphology of the particles. It has been found that $BaSnO_3$ crystallizes from an amorphous phase other than directly forming $BaSn(OH)_6$. The effects of the solvents on the crystallization of the powder have also been observed.

Acknowledgements The authors acknowledge Dr. M. Quilitz for the help with the final version of the manuscript.

References

1. Subbarao EC (1981) Ferroelectrics 35:143
2. Vivekanandan R, Kutty TRN (1988) Ceram Int 14:207
3. Wernicke R (1978) Ber Dtsch Keram Ges 55:356
4. Brauer H (1970) Z Angew Phys 29:282
5. Moseley PT, Williams DE, Tofield BC (1988) Sensor Actuator 14:79
6. Shimizu Y, Shimabukuro M, Arai A, Seiyama T (1989) J Electrochem Soc 136:1206
7. Lampe U, Gerblinger J, Meixner H (1995) Sensor Actuator B 24–25:657
8. Lampe U, Gerblinger J, Meixner H (1995) Sensor Actuator B 26–27:97
9. Cerda J, Morante JR, Spetz AL (2003) Sensors 2:1164
10. Aguas MD, Morris L, Parkin IP (2002) J Mater Sci 37:375
11. Tao S, Gao F, Liu X, Sorensen OT (2000) Sensor Actuator B 71:223
12. Chu X (2004) Mater Sci Eng B 106:305
13. Viviani M, Buscaglia MT, Buscaglia V, Leoni M, Nanni P (2001) J Europ Ceram Soc 21:1981
14. Reddy CVG, Panorama SV, Rao VJ (2001) J Mater Sci: Mater Electron 12:137
15. Sano H, Herber RH (1968) J Inorg Nucl Chem 30:409
16. Wagner G, Binder H (1958) Z Anorg Allegem Chem 297:328
17. Kutty TRN, Vivekanadan R (1987) Mat Res Bull 22:1457
18. Udawatte CP, Yoshimura M (2001) Mater Lett 47:7
19. Jaeger L, Volker L, Mueller T, Abicht H-P, Roessel M, Goerls H (2004) Z Anorg Allg Chem 630:189
20. Lu W, Schmidt H (2005) J Eur Ceram Soc 25:919
21. Dutta PK, Asiaie R, Akbar SA, Zhu W (1994) Chem Mater 6:1542
22. Chien AT, Speck JS, Lange FF, Daykin AC, Levi CG (1995) J Mater Res 10:1784
23. Sato S, Murakata T, Yanagi H, Miyasaka F (1994) J Mater Sci 29:5657
24. Heng CH, Ma J, Zhao Z, Qi L (1996) J Mater Sci Lett 15:1245
25. Lu C, Lo S, Lin H (1998) Mater Lett 34:172
26. Padmini P, Kutty TRN (1994) J Mater Chem 4:1875
27. Kaiser A, Berger A, Sporn D, Bertganolli H, Ceram Trans, vol 51: Ceram Proc Sci Tech, Am Ceram Soc, Inc. 1995, p 51
28. Avudaithai M, Kutty TRN (1987) Mat Res Bull 22:641
29. Chen D, Xu R (1998) J Mater Chem 8:965
30. Kutty TRN, Vivekanandan R (1988) Mater Chem Phys 19:534
31. Somiya S, Adv Ceram 3 (Meet.), 3rd (1990), Meeting date 1988, p 207
32. Lin J, Duh J (1997) J Am Ceram Soc 80:92
33. Schrerrer P, Gött. Nachrichten, conference on July 26, 1918, p 99
34. Buscaglia MT, Leoni M, Viviani M, Buscaglia V (2003) J Mater Res 18:560
35. Vivekanandan R, Kutty TRN (1988) Ceram Inter 14:207