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Lyothermal synthesis of nanocrystalline $BaSnO_3$ powders

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Abstract

The synthesis of $BaSnO_3$ powders has been investigated at lyothermal conditions (temperature of 250 °C; $t = 6$ h), starting from $SnO_2{\cdot}xH_2O$ and $Ba(OH)_2$ and methanol, ethanol, isopropanol and acetone as solvents. Among them isopropanol was found to be the most suitable medium for preparing $BaSnO_3$. By addition of the modifier Genapol X-080 during the processing, the BET specific surface area of the end-powder was increased by a factor of 10. The as-prepared powder consisted of $BaSn(OH)_6$. The thermal behavior, the crystallization behavior and the structure evolution of the powder during heating treatment have been studied with the TG–DTA–MS, XRD and FTIR. The weight loss of the as-prepared powder of about 12 wt% heated up to 1200 °C is mainly attributed to the dehydration around 260 °C which leads to the structure rearrangement and the building of the $[SnO_6]$ octahedra. At this temperature $BaSn(OH)_6$ converts to an amorphous phase, from which $BaSnO_3$ nucleates and grows with increasing temperature. The obtained $BaSnO_3$ powders had a BET specific surface area of 16.56 m^2/g and a primary crystallite size of 49 nm.

Keywords: A. Powders: chemical preparation; B. X-ray methods; C. Thermal properties; D. $BaSnO_3$

1. Introduction

With its characteristic dielectric properties perovskite-type $BaSnO_3$ has been used as a component of ceramic dielectric bodies to prepare thermally stable capacitors [1,2], and to fabricate ceramic boundary layer capacitors when combined with $BaTiO_3$ [3,4]. It was recently found that $BaSnO_3$ exhibits strong near-infrared luminescence at room temperature and could be a potential material for constructing NIR electroluminescent thin-film devices [5]. The application of $BaSnO_3$ 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 [6–15] has been reported.

$BaSnO_3$ powder is conventionally prepared by solid reaction through sintering $BaCO_3$ and SnO_2 at a high temperature ranging from 1200 °C to 1400 °C [16,17]. A hydrothermal synthesis route for preparation of $BaSnO_3$ was first reported by Kutty and Vivekanadan [18] and was investigated by other groups [19–21]. Starting from a tin oxide hydrate ($SnO_2{\cdot}xH_2O$), fine $BaSnO_3$ powders can be either prepared at 260 °C through a intermediate $BaSn(OH)_6$ or directly prepared at 330 °C with water as the medium of the hydrothermal reaction. Up to date no nonaqueous solvent as the medium of lyothermal synthesis for preparing $BaSnO_3$ powder has been reported. On the other hand, some ceramic oxide powders such as $BaTiO_3$ and $SrTiO_3$ have been synthesized via lyothermal reaction. It has been found [22] that using solvents such as alcohol or acetone can accelerate the synthesis reaction of $BaTiO_3$. Powders prepared in ethanol exhibited a more uniform particle size distribution. Isopropanol has been reported [23] to be the optimal medium by way of completion of the reaction to prepare $SrTiO_3$. Products of smaller particle size and low residual H_2O contents were obtained for higher isopropanol concentrations. Methanol or 2-methoxyethanol [24] also contributed to nanosized $PbTiO_3$ particles exhibiting a lower agglomeration and a narrow size distribution.

In the present paper the effects of the solvent on the properties of the resulting powders will be investigated. To limit agglomeration between particles, the controlled growth process technique [25–27] was employed during lyothermal synthesis. The thermal behavior, the crystallization behavior and the structure rearrangement of the obtained powder during heating treatment will be characterized and presented.

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2. Experimental procedure

The fresh tin oxide hydrate gel precipitated from $SnCl_4$ solution with ammonia solution was suspended in methanol, ethanol, isopropanol or acetone (0.3 M), and mixed with $Ba(OH)_2$ (the molar ratio of Ba:Sn was 1.10) by using argon as the protecting gas. The suspension was thereafter charged in a teflon-lined autoclave (Berghof) and treated under lyothermal conditions at 250 °C for 6 h. To limit agglomeration between the particles of the resulting powder, the lyothermal reaction was also carried out in the presence of a surface active agent (Genapol X-080, 5 wt%: Clariant, fatty alcohol polyglycol ether based on isotridecyl alcohol with about 8 mol ethoxyl). The educt was taken out at room temperature and washed with distilled water until its pH value was near 7. The powder dried at 60 °C in a vacuum oven was then calcined in a drying oven at 260 °C for a definite time.

The crystalline phase of the powder was analyzed with a D500 model diffractometer (Siemens, radiation Cu $K\alpha_1$) operating at 40 kV. The crystallite size was calculated by using Scherrer equation [28]. The thermal behaviors of the samples were analyzed through thermogravimetric and differential thermal analysis (TG–DTA: STA501, Baer) coupled with a mass spectrometer (MS: QMS420, Netzsch). The infrared spectra of the samples treated at various temperatures were recorded with a Fourier transform infrared spectrometer (FTIR: IFS 25v, Bruker) to analyze the structure evolution. The specific surface area of the powders was characterized with a BET gas adsorption analyzer (ASAP 2400, Micrometrics). The density of powder samples was measured by a gas pycnometer (Micrometrics).

3. Results and discussion

In the lyothermal reaction methanol, ethanol, isopropanol and acetone were used as the solvent, respectively. As the as-prepared powder resulting from lyothermal synthesis does not consist of barium stannate but barium tin hydroxide, it was then calcined in an oven at 260 °C for 4 h to realize the crystal phase conversion.

The FTIR spectra of the calcined powders are shown in Fig. 1. In the alcoholic series the $SnO_3{}^{2-}$ band [29] centered at 630 cm^{-1} intensifies with an increase in carbon atom number. As for acetone, the band is comparable to that of ethanol. The existence of the band of the Sn–OH group [30] around 500 cm^{-1} in methanol, ethanol and acetone indicates an incomplete conversion of $BaSn(OH)_6$ into $BaSnO_3$ in the corresponding powders. In the case of isopropanol, the Sn–OH band disappears. The broad OH band around 3300 cm^{-1} and the peak at 1640 cm^{-1} indicates water in the samples which is absorbed from the atmosphere either by $BaSnO_3$ powder or/and by the KBr pellet. The weak peak at 860 cm^{-1} indicates the small amount of carbonates in the powder. The carbonates can form with CO_2 absorbed from the atmosphere. Another characteristic peak of the carbonate at 1440 cm^{-1} has been integrated in the big band around 1440 cm^{-1}. This band seems to be correlated with a barium group because in most of barium compounds a peak at the same position can be found [29].

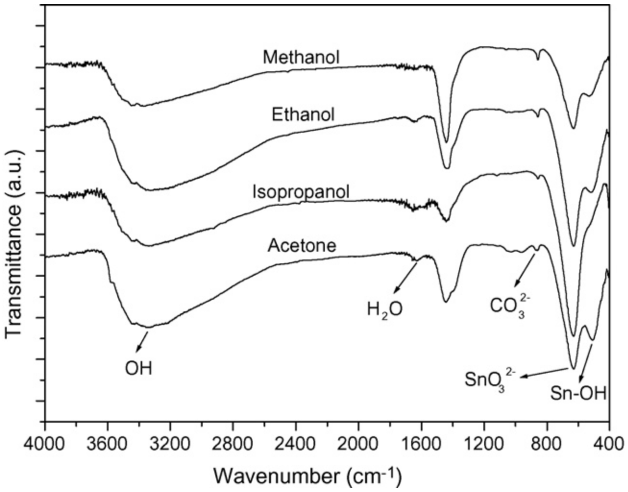

Fig. 1. FTIR spectra of the powders calcined at 260 °C for 4 h (KBr pellet). The powders were lyothermally synthesized by using different solvents as the medium at 250 °C for 6 h.

XRD patterns of the calcined powders are shown in Fig. 2. The powders synthesized in methanol, ethanol and acetone consist mainly of $BaSnO_3$, but $BaCO_3$ and an unknown phase can also be detected. In the case of isopropanol, only $BaSnO_3$ can be found, this means, the amount of the carbonate reflected in the corresponding IR spectrum is too small to be detected. By comparing the crystalline peaks of $BaSnO_3$, we can found their intensity increase according to the order: acetone < methanol < ethanol < isopropanol, which indicates among these solvents isopropanol is the best medium to promote the crystallization of $BaSnO_3$. Table 1 shows the influence of solvent on the properties of the powders calcined at 260 °C. The primary particle size of $BaSnO_3$ varies between 32 nm and 44 nm. The BET specific surface area of the powders is very small (only 1–3 m^2/g). The average particle diameter calculated from it is in the micrometer region. This means agglomeration between particles was

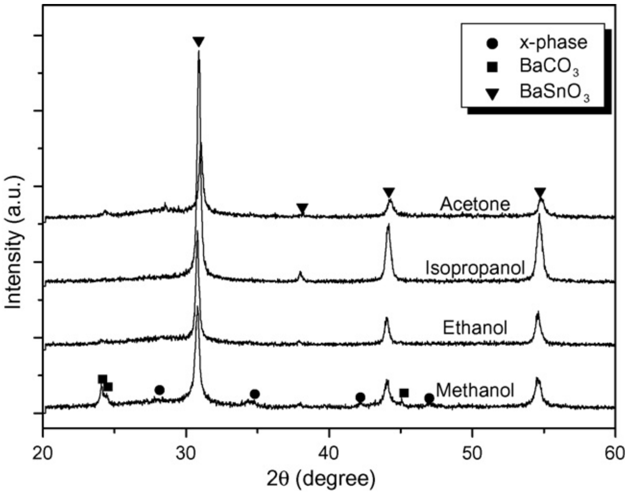

Fig. 2. XRD patterns of the powders calcined at 260 °C for 4 h. The powders were lyothermally synthesized at 250 °C for 6 h by using different solvents as the medium.

Table 1
Properties of the powders calcined at 260 °C for 4 h vs. solvent

Properties of sample	Primary crystallite size (nm)	BET specific surface area (m^2/g)	Density (g/cm^3)	Average particle diameter (nm)
Methanol	32	1.23	5.08	960
Ethanol	44	2.51	5.37	445
Isopropanol	41	1.74	5.57	619
Acetone	35	2.66	5.09	443

The powders were lyothermally synthesized at 250 °C for 6 h. Primary crystallite size is calculated from XRD patterns according Scherrer equation. Average particle diameter (d) is calculated from density (D) and surface area (S) according to $d = 6/DS$.

very severe. A maximal density of the powder (5.57 g/cm^3) is achieved by using isopropanol as the solvent.

As pure $BaSnO_3$ powders with better crystallization can be lyothermally prepared from isopropanol, isopropanol is therefore more suitable for preparing barium stannate than the other three solvents. To limit particle agglomeration, Genapol X-080 was added in the system using isopropanol as the medium for synthesizing $BaSnO_3$ powder.

Fig. 3 shows the TG–DTA–MS curves of the powder lyothermally synthesized at 250 °C for 6 h in isopropanol with 5 wt% Genapol X-080 (relative to the formed $BaSnO_3$ powder) as the surface modifier. The endothermic peak at 260 °C in the DTA curve (Fig. 3a) can be definitely attributed to the dehydration of the powder because a water release peak is found at the same position in the MS curve (Fig. 3b). The exothermic peak at 520 °C in the DTA curve is thought to be the recrystallization peak of $BaSnO_3$. Corresponding to the dehydration of powder, a weight loss of 9.5 wt% up to 400 °C is found in the TG-curve (Fig. 3a). The weight loss becomes slower but continues up to 1000 °C. From 1000 °C on little weight change can be observed. The total weight loss of the sample until 1200 °C is 12.4 wt%. As the as-prepared powder is regarded as a hydrate of $BaSnO_3$ and notes as $BaSnO_3{\cdot}xH_2O$, the x value calculated from the TG curve is 2.39. In the MS curve another CO_2 peak at 780 °C is also observed. The release of CO_2 gas from the powder can result from the reaction between tin oxide and $BaCO_3$ as following [31]:

$$BaCO_3 + SnO_2 \rightarrow BaSnO_3 + CO_2\uparrow \qquad (1)$$

Fig. 4 presents the XRD patterns of this powder calcined at different temperatures. The as-prepared powder consists of $BaSn(OH)_6$. It converts to an amorphous phase at 260 °C after 4 h of calcinations. As the calcining temperature is increased to 330 °C, $BaSnO_3$ forms. At the same time traces of $BaCO_3$ can be found in the powder. As the calcining time being extending from 4 h to 10 h, $BaSnO_3$ crystallizes more completely. The results reveal that $BaSnO_3$ does not transform directly from $BaSn(OH)_6$ but from an intermediate amorphous phase. Compared with Fig. 2, it can be found that addition of the surfactant Genapol X-080 impedes the transformation of $BaSnO_3$ from

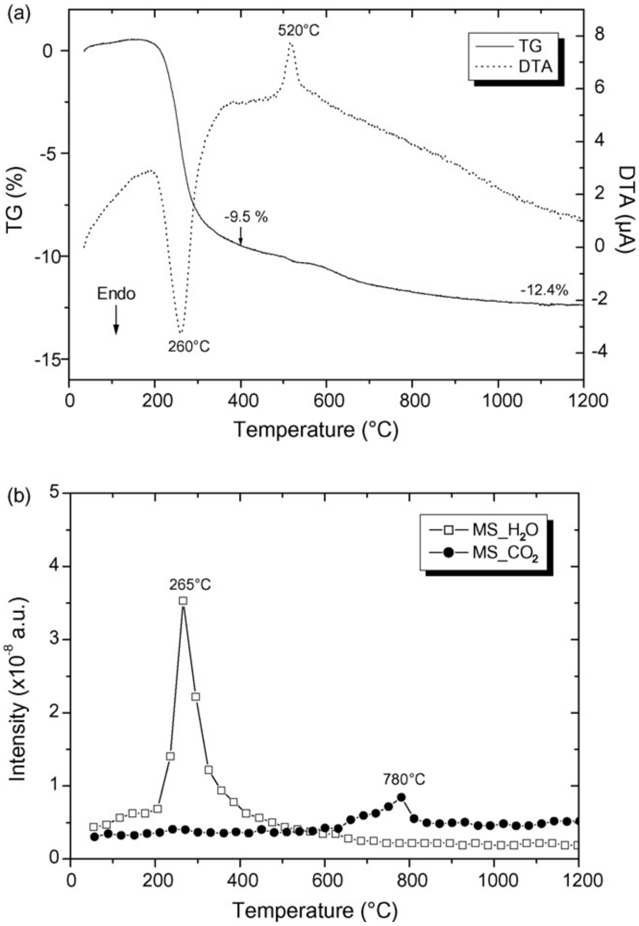

Fig. 3. (a) TG–DTA, (b) MS curves of the as-prepared powder synthesized in isopropanol at 250 °C for 6 h in the presence of 5 wt% Genapol X-080. Heating rate is 10 °C/min.

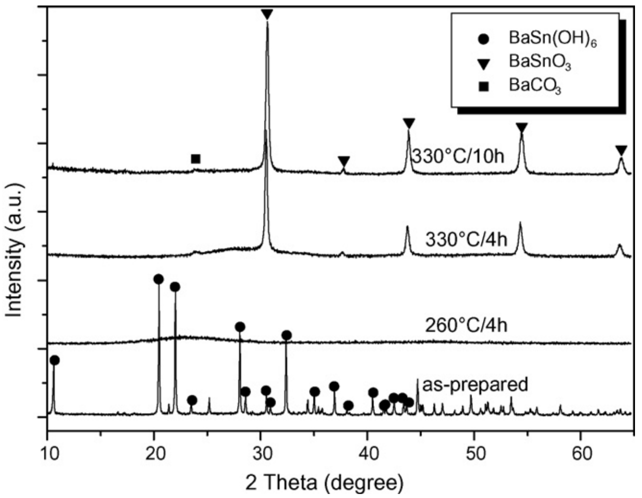

Fig. 4. XRD patterns of the powder lyothermally synthesized in isopropanol at 250 °C for 6 h in the presence of 5 wt% Genapol X-080 for various temperature and duration of calcination.

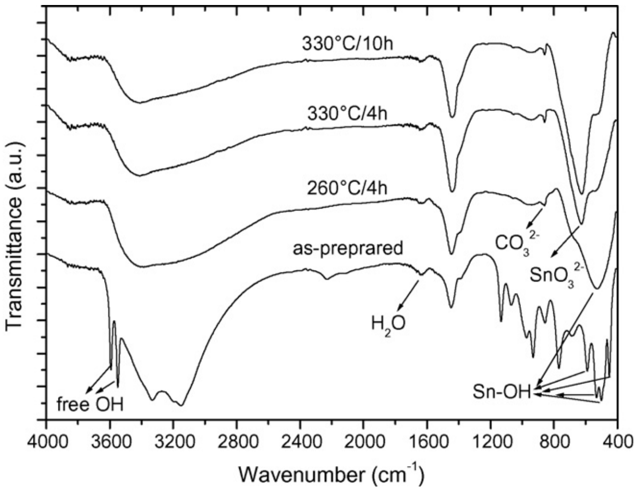

Fig. 5. FTIR spectra of the powder lyothermally synthesized in isopropanol at 250 °C for 6 h in the presence of 5 wt% Genapol X-080 for various temperature and duration of calcination (KBr pellet).

$BaSn(OH)_6$ and results in an higher crystallization temperature. The primary crystallite size of $BaSnO_3$ at 330 °C/10 h is 49 nm.

The molecular structure of the powder modified with Genapol X-080 versus calcining temperature can be seen in Fig. 5. The Sn–OH band in the as-prepared powder around 500 cm^{-1} consists of 4 peaks. The free OH groups near 3600 cm^{-1} are obvious. After the powder being calcined at 260 °C for 4 h, the 4-set peaks of Sn–OH round off and the free OH groups disappear whereas a CO_3^{2-} band appears. A SnO_3^{2-} band appears after the powder was calcined at 330 °C for 4 h. The intensity of this peak increases with increasing the time from 4 h to 10 h. The change of the spectra reflects the structure rearrangement of the powder during heat treatment. The dehydration of the powder at 260 °C leads to the rounding off of the Sn–OH band and the disappearance of the free OH groups. As a result, an amorphous phase forms. Further increasing the calcining temperature contributes to the building of $[SnO_6]$ at the cost of Sn–OH. That is, $BaSnO_3$ nucleates and grows with increasing calcining temperature and time.

The density of the $BaSnO_3$ powder obtained at 330 °C for 10 h in the presence of 5 wt% Genapol X-080 is 5.25 g/cm^3 and has a BET specific surface of 16.56 m^2/g. The average particle size of 69 nm calculated from the specific surface and the density is near the primary crystallite size (49 nm). This indicates that the surfactant can effectively limit the agglomeration between particles and therefore increase the surface area of the $BaSnO_3$ powder.

4. Summary

Nanocrystalline $BaSnO_3$ powder has been prepared by lyothermal synthesis at 250 °C. The solvent used in the lyothermal reaction can affect the composition, the surface area and the density of the resulting powder, as well as the crystallization and the primary particle size of $BaSnO_3$. The powder derived from isopropanol shows high purity and is well-crystallized. Therefore isopropanol is more suitable for preparing $BaSnO_3$ powder than the other solvents under investigation. The addition of Genapol X-080 as modifier has limited the agglomeration of the particles and lead to an increase in BET specific surface area of the $BaSnO_3$ from 1.74 m^2/g to 16.56 m^2/g. However, the crystallizing temperature of $BaSnO_3$ has to be improved from 260 °C to 330 °C. Investigation on the crystallization behavior shows that in the presence of the surfactant $BaSn(OH)_6$ transforms at 260 °C into an amorphous phase which converts into $BaSnO_3$ at 330 °C.

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References

[1] E.C. Subbarao, Ceramic dielectrics for capacitors, Ferroelectrics 35 (1981) 143–148.
[2] R. Vivekanandan, T.R.N. Kutty, Hydrothermal synthesis of $Ba(Ti, Sn)O_3$ fine powers and dielectric properties of the corresponding ceramics, Ceram. Int. 14 (1988) 207–216.
[3] R. Wernicke, Influence of microstructure on the electrical properties of intergranular capacitors, Ber. Dtsch. Keram. Ges. 55 (1978) 356–358.
[4] H. Brauer, Grain-boundary barrier layers in barium metatitanate ceramic with a high effective dielectric constant (Ger.), Z. Angew. Phys. 29 (1970) 282–287.
[5] H. Mizoguchi, P.W. Woodward, C. Park, D.A. Keszler, Strong near-infrared luminescence in $BaSnO_3$, J. Am. Chem. Soc. 126 (2004) 9796–9800.
[6] P.T. Moseley, D.E. Williams, B.C. Tofield, Electrical conductivity and gas sensitivity of some transition metal tantalates, Sens. Actuators 14 (1) (1988) 79–91.
[7] Y. Shimizu, M. Shimabukuro, H. Arai, T. Seiyama, Humidity-sensitive characteristics of lanthanum(3+)-doped and undoped strontium tin oxide ($SrSnO_3$), J. Electrochem. Soc. 136 (4) (1989) 1206–1210.
[8] U. Lumpe, J. Gerblinger, H. Meixner, Carbon-monoxide sensors based on thin films of $BaSnO_3$, Sens. Actuators B 24/25 (1995) 657–660.
[9] U. Lumpe, J. Gerblinger, H. Meixner, Nitrogen oxide sensors based on thin films of $BaSnO_3$, Sens. Actuators B 26/27 (1995) 97–98.
[10] J. Cerda, J.R. Morante, A.L. Spetz, $BaSnO_3$ oxygen sensors without the need of a reference electrode, Sensors 2 (2003) 1164–1165.
[11] M.D. Aguas, L. Morris, I.P. Parkin, Self-propagating solid state routes to $BaSnO_3$; investigation of gas sensing properties, J. Mater. Sci. 37 (2002) 375–379.
[12] S. Tao, F. Gao, X. Liu, O.T. Sorensen, Ethanol-sensing characteristics of barium stannate prepared by chemical precipitation, Sens. Actuators B 71 (2000) 223–227.
[13] X. Chu, Dilute CH_3SH-sensing characteristics of $BaSnO_3$ thick film sensor, Mater. Sci. Eng. B 106 (2004) 305–307.
[14] M. Viviani, M.T. Buscaglia, V. Buscaglia, M. Leoni, P. Nanni, Barium perovskites as humidity sensing materials, J. Eur. Ceram. Soc. 21 (2001) 1981–1984.
[15] C.V.G. Reddy, S.V. Manorama, V.J. Rao, Preparation and characterization of barium stannate: application as a liquefied petroleum gas sensor, J. Mater. Sci.: Mater. Electron. 12 (2001) 137–142.
[16] H. Sano, R.H. Herber, Moessbauer parameters of barium stannate, J. Inorg. Nucl. Chem. 30 (2) (1968) 409–413.
[17] G. Wagner, H. Binder, Herstellung von Bariumstannat (Ger.), Z. Anorg. Allg. Chem. 297 (1958) 328–346.
[18] T.R.N. Kutty, R. Vivekanadan, $BaSnO_3$ fine powders from hydrothermal preparation, Mater. Res. Bull. 22 (11) (1987) 1457–1465.
[19] C.P. Udawatte, M. Yoshimura, Preparation of well-crystallized $BaSnO_3$ powders under hydrothermal conditions, Mater. Lett. 47 (2001) 7–10.
[20] L. Jaeger, L. Volker, T. Mueller, H. Abicht, M. Roessel, H. Goerls, Barium stannate powders form hydrothermal synthesis and by thermolysis of

barium-tin (IV)–glycolates. Synthesis and structure of $[Ba(C_2H_6O_2)_4]$ $[Sn(C_2H_4O_2)_3]$ and $[Ba(C_2H_6O_2)_2]$ $[Sn(C_2H_4O_2)_3]\cdot CH_3OH$, Z. Anorg. Allg. Chem. 630 (2004) 189–195.

[21] W. Lu, H. Schmidt, Hydrothermal synthesis of nanocrystalline $BaSnO_3$ using a $SnO_2\cdot xH_2O$ sol, J. Eur. Ceram. Soc. 25 (2005) 919–925.

[22] P. Padmini, T.R.N. Kutty, Wet chemical synthesis of ultrafine multicomponent ceramic powders through gel to crystallite conversion, J. Mater. Chem. 4 (12) (1994) 1875–1881.

[23] M. Avudaithai, T.R.N. Kutty, Ultrafine powders of $SrTiO_3$ from the hydrothermal preparation and their catalytic activity in the photolysis of water, Mater. Res. Bull. 22 (1987) 641–650.

[24] D. Chen, R. Xu, Solvothermal synthesis and characterization of $PbTiO_3$ powders, J. Mater. Chem. 8 (4) (1998) 965–968.

[25] H. Schmidt, Materials in nanotechnology, in: H. Meixner, R. Jones (Eds.), Sensors vol. 8, Micro- and Nanosensor Technology: Trends in Sensor Markets, VCH, Weinheim, 1995, pp. 275–293.

[26] H. Schmidt, Relevance of sol–gel methods for synthesis of fine particles, Kona Powder Particle 14 (1996) 92–103.

[27] H. Schmidt, Chemistry and technology of nanoparticles: preparation, processing and application, in: European Conference on Advanced Materials and Processes and Applications [EUROMAT]: Proceedings, vol. 3: Surface Engineering and Functional Materials, Maastricht, NL, (1997), pp. 5–10.

[28] P. Schrerrer, Goett. Nachrichten, Conference on July 26, 1918, pp. 99–100.

[29] The Infrared Spectra Handbook of Inorganic Compounds, Bio Rad, Sadtler Division, USA, 1984.

[30] S.J.L. Ribeiro, C.V. Santilli, S.H. Pulcinelli, F.L. Fortes, L. Oliveira, Spectroscopic characterization of SnO_2 gels, J. Sol–Gel Sci. Technol. 2 (1–3) (1994) 263–267.

[31] C.P. Udawatte, M. Kakihana, M. Yoshimura, Preparation of pure perovskite-type $BaSnO_3$ powders by the polymerized complex method at reduced temperature, Solid State Ionics 108 (1998) 23–30.