Journal of the European Ceramic Society **17** (1997) 1453–1457

PII: S0955-2219(97)00002-2
0955-2219/97/$17.00

Characterization of $BaSnO_3$ Powder Obtained by a Modified Sol–Gel Route

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(Received 22 May 1996; revised version received 26 November 1996; accepted 2 December 1996)

Abstract

A modified sol–gel method is used to prepare stoichiometric, homogeneous barium stannate powders. The synthesis process is described in detail in this paper. One of the main characteristics of this process is that monophasic powders are obtained easily at low temperature (1000°C). The resulting powders are characterized by several methods such as X-ray diffraction, scanning electron microscopy, X-ray analysis, infrared spectroscopy and thermogravimetric analysis. The different characterizations allow us to conclude that powders obtained by this method contain no impurity. These conclusions show that this process is ideal for obtaining fine powders that will give dense ceramics. © 1997 Elsevier Science Limited.

1 Introduction

Barium stannate has found increasing applications in materials technology as a constituent in perovskite solid solutions with complex compositions. Stannates have received most attention in recent years as components of ceramic dielectric bodies.[1] In fact, stannates of general formula $MSnO_3$, where M = Ca, Sr and Ba, form a component of dielectric materials used for thermally stable capacitors.[2] $BaSnO_3$–$BaTiO_3$ binary systems are very important in the fabrication of ceramic multilayer capacitors.[3] Porous $Ba(Ti,Sn)O_3$ ceramic materials are used in the preparation of multifunctional temperature–humidity–gas sensors.[4]

The ceramic method of preparing monophasic $BaSnO_3$ from $BaCO_3$ and SnO_2 requires temperatures as high as 1380°C.[5] These powders always contain impurities and are coarse grained. Coffeen[6] has reported the preparation of $BaSnO_3$ involving the coprecipitation of hydrated barium meta stannate, $BaSnO_3 \cdot 3H_2O$ from basic solutions. However, Savos'kina *et al.*[7] observed that during this coprecipitation, along with the formation of hydrated $BaSnO_3$, a solid barium tin hydroxide is also formed, so that on heating at 1000°C, phase-purity of $BaSnO_3$ is often very difficult to achieve.

To study the electric properties of $BaSnO_3$, we need ceramics with high purity and good density. It is well known that the sol–gel method is superior to the conventional solid state reaction because in the former it is possible to mix the starting materials at the molecular level and the resulting product is expected to be homogeneous. No sol–gel preparation of $BaSnO_3$ has been reported up to now. Among the numerous processes developed for producing ceramic oxide powders, some of them use organic polymers as intermediate auxiliaries between a precursor solution and the oxide powder. Pechini[8] first prepared perovskite powders by dispersing metallic cations in a polyester resin resulting from polycondensation between ethylene glycol and citric acid. Micheli[9] has described the precipitation of metal polyacrylate which affords ultrafine powders with high specific surface areas. Another process[10] has been described, where an organic polymeric network, the polyacrylamide gel, is just used for solidifying a stable aqueous solution where the cations are complexed by citric acid. Our investigations on the formation of $BaSnO_3$ have shown that better results are obtained with the last process if we modify some procedures. This paper describes in detail the synthesis procedures needed to obtain fine and homogeneous powders of $BaSnO_3$ with high purity by the modified sol–gel route. The obtained powders are characterized by several techniques such as X-ray diffraction, scanning electron microscopy, X-ray analysis, thermogravimetric (TGA) measurements and infrared analysis.

2 Process of Synthesis

The sol–gel method[10] used to prepare barium stannate has been modified. This process consists of gelation of an aqueous solution containing the

appropriate ratios of the required elements through an organic polymer network. Oxide ceramics may be obtained chemically in this way.[11,12] The resulting powders are extremely homogeneous and fine. Generally the synthesis temperature is less elevated than in the case of a solid state reaction. Another important point is that some compounds have been synthesized without any segregation only by this sol–gel process.[13] Our goal being to easily prepare homogeneous powders of barium stannate at low temperature, we decided to investigate this process. The starting materials are tin chloride and barium carbonate. An aqueous solution is first made by dissolving the tin salt in distilled water. The stability of the solution against hydrolysis or condensation is improved by complexing the cations by a chelating agent such as citric acid $C_6H_8O_7.H_2O$, using one formula unit per valence of each cation. $BaCO_3$ is then added to the solution. An appropriate amount of chelating agent is added (one equivalent of citric acid per valence of ion). The quantity of $BaCO_3$ introduced into the solution is such that the ratio of the molar number of barium and tin is equal to unity. The final solution is stabilized by homogenization. After 15–30 min the clear solution is then neutralized by addition of ammonia. In the basic process the pH is adjusted to pH 2–3. In the case of $BaSnO_3$, no clear solution is obtained if the pH is acid so the solution is neutralized. In 100 ml of the clear fresh aqueous solution containing Sn and Ba in stoichiometric ratios, 6 g of acrylamide and 0·8 g of *N,N,N′,N′*- tetramethylethylenediamine (Temed, Merck) are first dissolved. The solution is heated over a boiling water bath with magnetic stirring and, as soon as the temperature reaches 80°C, *N,N′*-methylene-bis-azobisisobutyronitrile (AIBN) (0·1 g) is introduced; gelation occurs within a few minutes. This aqueous gel is transformed into a powder by calcination in air at 600°C for 5 h. The white powder formed is ground in an agate mortar. The powders are annealed in a platinum crucible at 1000°C for 17 h in air.

The aqueous precursor solution is gelled by *in situ* formation of a hydrophilic polymeric polyacrylamide network. The radical polymerization is initiated by free radicals brought by azobisisobutyronitrile and by temperature and is promoted by radical transfer agents such as *N,N,N′,N′*-tetramethylethylenediamine.

3 Characterization of the Resulting Powders

3.1 Crystallographic characterization

The resulting powders were identified from X-ray powder diffraction patterns recorded at room temperature with a Philips PW1729 diffractometer, using CuK_α, radiation. The X-ray powder diffraction pattern of the final product is shown in Fig. 1. Table 1 shows the observed and calculated $d(h,k,l)$ for $BaSnO_3$ compound. Cell parameter calculations were performed from the data of diffractograms. The compound was identified as a cubic perovskite-like phase. X-ray diffraction patterns could be indexed on the basis of a cubic unit cell having a lattice parameter of 4·117(1) Å. Smith and Welch reported a similar value: a = 4·117(2) Å.[14] and Megaw obtained a = 4·1168(2) Å.[15] We note good agreement with our value. No trace of any impurity phase was observed on our diffraction patterns and all the diffraction peaks can be indexed to the perovskite structure without any ambiguity.

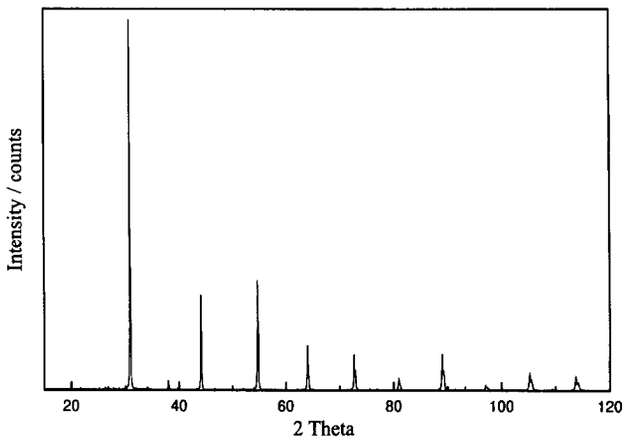

Fig. 1. X-ray powder diffraction pattern of $BaSnO_3$.

3.2 Scanning electron microscopy and X-ray analysis

The microstructure is a very important factor which must be controlled during the elaboration of the powder. Figure 2 shows $BaSnO_3$ powder obtained after the first calcination at 600°C. The powder has a leaf-shape. After heating at 1000°C

Table 1. Comparison of observed and calculated $d(h, k, l)$ for $BaSnO_3$

X-ray diffraction data for $BaSnO_3$; cubic, a = *4·117(2) Å*			
(h, k, l)	$2\theta_{obs}$(Å)	d_{obs}(Å)	d_{cal}(Å)
1 0 0	21·57	4·1163	4·1165
1 1 0	30·69	2·9107	2·9109
1 1 1	37·81	2·3773	2·3775
2 0 0	43·95	2·0583	2·0585
2 1 1	54·55	1·6808	1·6789
2 2 0	63·90	1·4556	1·4554
3 1 0	72·55	1·2997	1·2999
2 2 2	80·94	1·1870	1·1872
3 2 1	88·87	1·1002	1·0991
4 0 0	96·89	1·0290	1·0292
3 3 0	105·07	0·9702	0·9704
3 3 1	113·59	0·9444	0·9445

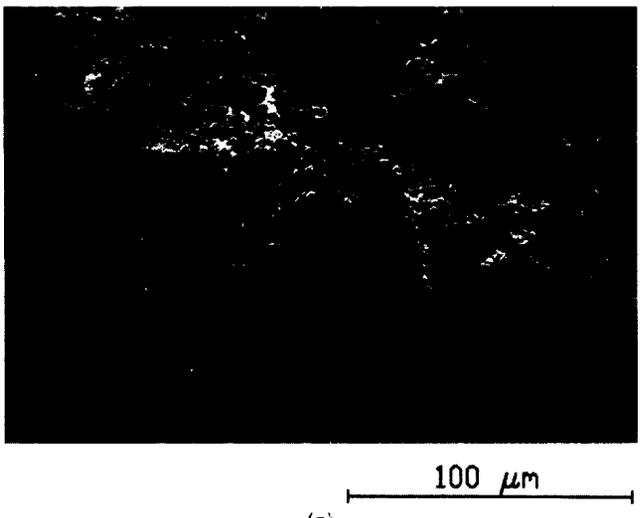

Fig. 2. Scanning electron micrograph of $BaSnO_3$ powder calcined at 600°C.

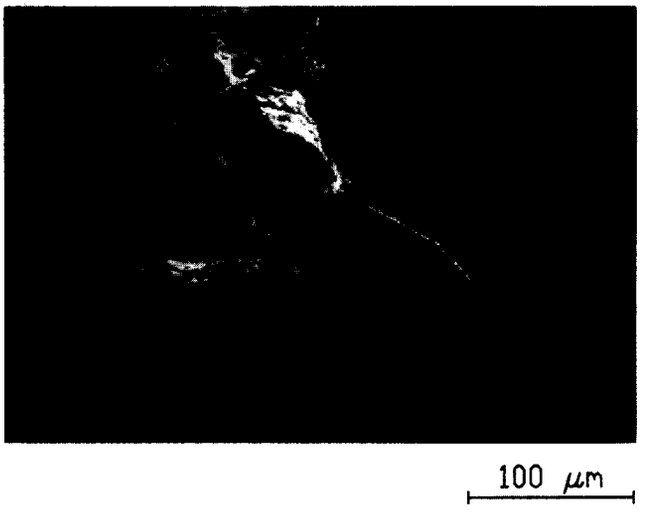

Fig. 3. (a) Scanning electron micrograph of $BaSnO_3$ powder obtained by modified sol–gel route after heating at 1000°C. (b) Scanning electron micrograph of $BaSnO_3$ powder obtained by solid state reaction.

this aspect disappears (Fig. 3(a)). Figure 3 shows the difference between the powder obtained by a solid state reaction and by the modified sol–gel process described in this paper. The solid state reaction gives powders with an irregular grain size (2–15 μm) whereas the single crystalline grain size of the modified sol–gel process powder is about 5 μm (Fig. 4). To check the homogeneity of the powders, X-ray analysis tests have been performed. No segregation of barium or of tin was revealed.

3.3 Infrared reflection spectroscopy

An infrared reflectivity spectrum has been recorded on a powder sample previously compacted and pressed under 4 kbar. A diopter is then obtained. Although its optical quality is poor, it is sufficient to minimize light scattering and keep a pseudo-specular configuration as soon as the wavelength of the incident radiation remains in the far-infrared. The experiments have been performed in

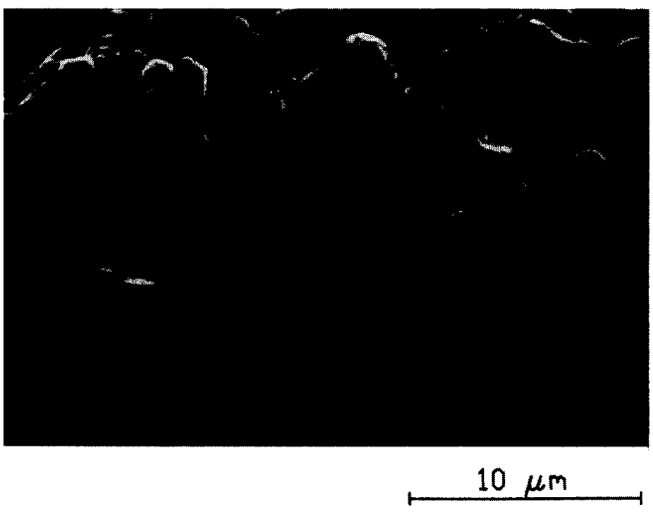

Fig. 4. Scanning electron micrograph of $BaSnO_3$ powder calcined at 1000°C.

the wave-number range 10–1500 cm^{-1} with a Bruker IFS 307 Fourier-transform spectrometer. Three main reflection bands are observed in the

$BaSnO_3$ spectra (Fig. 5). This spectrum is similar to that observed for a cubic perovskite structure in accordance with group theory predictions. For the cubic perovskite the normal modes of the lattice vibration at the zone centre are given in the irreducicible representation by:

$$\Gamma^{\text{total}} = 4\ F_{1u} + F_{2u}$$

One of the F_{1u} modes corresponds to the acoustic phonon mode and the F_{2u} mode is optically silent, i.e. it is neither IR nor Raman active. The remaining three F_{1u} modes are IR active, corresponding, respectively, to the following vibrational motions: Sn–O bond distance modulation (stretching mode), translational motion of barium atoms with respect to the SnO_3 lattice (external mode) and Sn–O bond angle modulation (bending mode). In the absence of single-crystal data or dense ceramic data, we did not attempt conventional treatments of the reflectivity spectra by Kramers–Kronig analysis or fitting with a dielectric function model. This study on ceramics will be realized in a future work. The two main bands characteristic of barium carbonate at 870 and 1430 cm^{-1} are not observed in our spectrum. We can therefore conclude that the powder exhibits no trace of barium carbonate. This result is in agreement with our X-ray diffraction results.

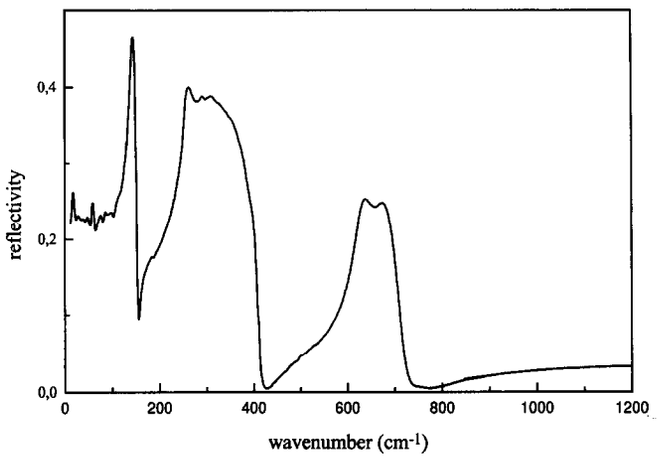

Fig. 5. Infrared reflection spectra of $BaSnO_3$.

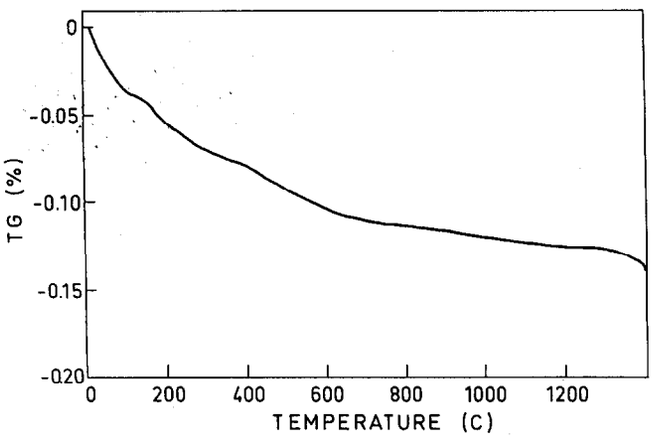

Fig. 6. Thermogravimetric curve of $BaSnO_3$ powder.

3.4 Thermogravimetric measurements

Thermogravimetric measurements were made with a Setaram thermobalance, under air. Approximately 80 mg of powder were weighed in a platinum crucible. The temperature was raised from room temperature up to 1400°C at 5°C/min. TGA measurements are shown in Fig. 6 and gave a curve with two weight losses: the first near 80°C resulting from absorbed water removal and the second between 370°C and 800°C, which can be due to the CO_2 release during $BaCO_3$ decomposition. In this case the weight loss was estimated to be about 0·13%. There is no further weight loss in the TGA curve up to 1400°C. The amount of CO_2 detected by TGA only is probably due to carbonation of the compound in air.

4 Conclusions

This paper reports a new way of obtaining barium stannate powders with high purity. This method is based on a polyacrylamide gel process, using aqueous solutions. The synthesis procedures of the basic process have been modified, and are described in detail.

It is important to note that (i) for the first time we report a synthesis method based on a sol–gel process, which enables pure $BaSnO_3$ to be obtained easily: phase purity has often been very difficult to achieve up to now;[6,7] (ii) stoichiometric barium stannate powders are obtained at moderately elevated temperature (1000°C): to our knowledge, the synthesis of pure $BaSnO_3$ at such a low temperature has not been reported in the literature. The results are interesting because the powders obtained are fine, homogeneous, pure and the synthesis temperature is moderate. So the densification is better (the first results are 98–99%) and easier to achieve. The optimization of the synthesis method is the first important step in the study of electrical properties. Future work will include the study of the influence of this elaboration method on the dielectric properties.

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