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Sol-gel synthesis and characterization of barium titanate powders

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A simple aqueous sol-gel route has been refined to prepare yttrium-doped barium titanate powders. Thermal decomposition of the fabricated gel was studied by means of DTA/TGA measurements. The precursor gel was intermediate calcined at 600 °C, and the final synthesis products were characterized by IR spectroscopy, X-ray powder diffraction and scanning electron microscopy. The barium titanate obtained from the calcination of the gel at 1300 °C was a tetragonal phase, and showed a positive temperature coefficient of resistivity (PTCR) effect which depends on sample cooling rate during the final heat treatment. © *1999 Kluwer Academic Publishers*

1. Introduction

Perovskite barium titanate ceramics are of interest owing to their ferroelectric and dielectric properties. The fabrication of positive temperature coefficient of resistivity (PTCR) materials has received considerable attention due to their specific applications, and among these materials the doped barium titanate continues to be widely investigated [1–8]. The PTCR effect is characterized by a rapid increase in electrical resistance as the temperature is increased over the ferroelectric transition temperature (Curie point). PTCR $BaTiO_3$ is used in a wide variety of applications, such as current limiters, constant temperature heaters and thermal sensors. Besides, the micro PTCR components are used for the investigation of heat exchange processes in plants and living organisms [9–13]. As a consequence of their wide application there is continued interest in the development of new synthetic methods.

The traditional solid-state synthesis of barium titanate ceramics involves the physical mixing of high-purity $BaCO_3$ and TiO_2 powders, sintering at high temperatures, grinding and re-sintering [8, 14, 15]. The high temperatures and long reaction times are necessary to overcome slow solid state diffusion since physical mixing can never be on the atomic scale. It is for this reason that chemical routes to barium titanate ceramics have become more extensively investigated. The solution chemical routes including sol-gel processing or thermal decomposition of metal alkoxides [12, 16–18], coprecipitation of mixed-metal oxalates [1, 19–21], or citrates [15, 22], hydrothermal synthesis [23, 24], spray-pyrolysis technique [25], and calcination of different barium titanium complexes [26–28] have potential advantages over the traditional solid-state reaction method. The phase purity and homogeneity of the product can be enhanced even at lower temperatures using chemical routes to barium titanate ceramics. Despite the advantages of these wet chemical syntheses, there are a number of significant difficulties, including: (i) strict control of reaction temperature; (ii) long synthesis procedures; (iii) barium titanium alkoxides require inert atmosphere; (iv) use of corrosive $TiCl_4$; (v) in some cases an expensive technique is used.

In our previous studies the simple aqueous sol-gel process to synthesize pure and europium and iron substituted $YBa_2Cu_4O_8$ superconducting samples has been described [29–31]. This sol-gel technique, starting from an aqueous acetate solution of Ba, Ca and Cu was suitable for synthesizing of precursors for the preparation of Hg-containing superconductors [32–34].

The purpose of the present work was to refine a simple and reliable sol-gel route using acetate/tartrate polymerized gels for preparing of PTCR yttrium doped barium titanate ceramics. The preparation of the gel precursors, and the characterization of the precursor, intermediate products and the final barium titanate powders are described here.

2. Experimental

Analytical grade $Ba(CH_3COO)_2$, Y_2O_3 and TiO_2 were used as the starting materials for the synthesis of precursors for yttrium doped barium titanate ceramics. Yttrium oxide (0.03 mmol) was first dissolved in 20 ml of 0.2M CH_3COOH. After stirring the mixture for 2 h at 65 °C in a beaker covered with a watch-glass a clear solution was obtained. Next, $Ba(CH_3COO)_2$ (9.97 mmol) was added and the solution was stirred for 2 h at the

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same temperature. Different amounts (0.3–1.2 g) of tartaric acid as complexing agent, dissolved in 20 ml of distilled water, were then added to the reaction solution. To this was added a mixture of TiO_2 (10 mmol) in 10 ml of 0.2M CH_3COOH. Finally, small amounts of 10% poly(vinyl alcohol) (PVA) (2–15 ml) as esterification agent was added to the above solution, and stirred for 1–24 h at 60–90 °C. After concentrating the solution for 5 h at 65 °C in an open beaker under stirring, a white monolithic gel was formed. White gel powders were obtained by drying the gel in a furnace at 90 °C. The gel powders were calcined in air at 900 °C. After an intermediate grinding the powders were sintered at 1300 °C for 5 h in air, and then cooled down to 900 °C at a cooling rate of 20–100 °C h^{-1} followed by furnace-cooling to room temperature.

The amount of barium in the samples was determined by the atomic absorption spectroscopic method (AAS, Hitachi 170-50). The titanium content was measured by ultraviolet spectrophotometry (SF 46) using hydrogen peroxide as a colouring agent. The thermal decomposition processes of the precursor gel were studied in a flowing oxygen atmosphere by thermogravimetric and differential thermal analyses using a Stanton-Redcroft TGA-DTA apparatus at a heating rate of 5 °C min^{-1}. For the IR spectroscopic measurement, the samples were mixed (1.5%) with dried KBr and pressed into the pellets. A Specord 75-IR spectrometer was used for the IR studies. The synthesized samples were characterized by X-ray powder analysis performed with a Stoe STADI P diffractometer, using CuK_{α_1} radiation. Scanning electron microscopy (SEM) was used for investigation of the morphology of the obtained materials. SEM studies were performed on a JEOL 820 scanning electron microscope. Resistivity measurements were carried out using a standard four-point dc technique after abrading the prepared specimens.

3. Results and discussion

To ascertain the homogeneity of the precursor gel, the optimization of the sol-gel process was made. The effect of experimental conditions was studied as follows: (i) molar ratio of tartaric acid to barium; (ii) the amount of PVA; (iii) reaction temperature; (iv) reaction time. The tartrate ligands form stable [35] and sufficiently soluble complexes with Ba^{2+} ions to prevent the crystallization of barium acetate. The observed critical limits for the $C_4H_6O_6 : Ba$ ratio are 0.25 and 0.65, restricted by the solubilities of barium acetate and tartrate, respectively. Thus, for the further experiments a $C_4H_6O_6 : Ba$ ratio of 0.45 was selected. The mixing of titania slurry with PVA solution yielded at first a colourless colloidal suspension. The chemical analysis of the obtained colloidal solution showed that the values for the barium and titanium contents depends on the PVA concentration, reaction temperature and time. The desirable Ba : Ti molar ratio of 1 : 1 was achieved when 8 ml (about 14% of the total volume) of the 10% PVA solution was added, and the resultant solution was stirred for 24 h at 65 °C in a beaker covered with a watch-glas. With continued heating at the same temperature in an open beaker, the solution became more viscous, i.e., the gelation and syneresis reactions took place, resulting in the formation of a white monolithic gel.

Sols and gels are usually considered as intermediates in the processing of glasses and ceramics. Therefore, drying and densification are very important stages of their synthesis. The characterization of precursor gels gives a better understanding of and allows control of the whole process of synthesis. The mechanism of the thermal decomposition of dried gel was studied in an argon atmosphere by means of DTA/TGA measurements in the temperature range 20–1000 °C. Fig. 1 shows the DTA/TGA curves for the ternary barium, yttrium and titanium over-dried gel. The gel powders show an

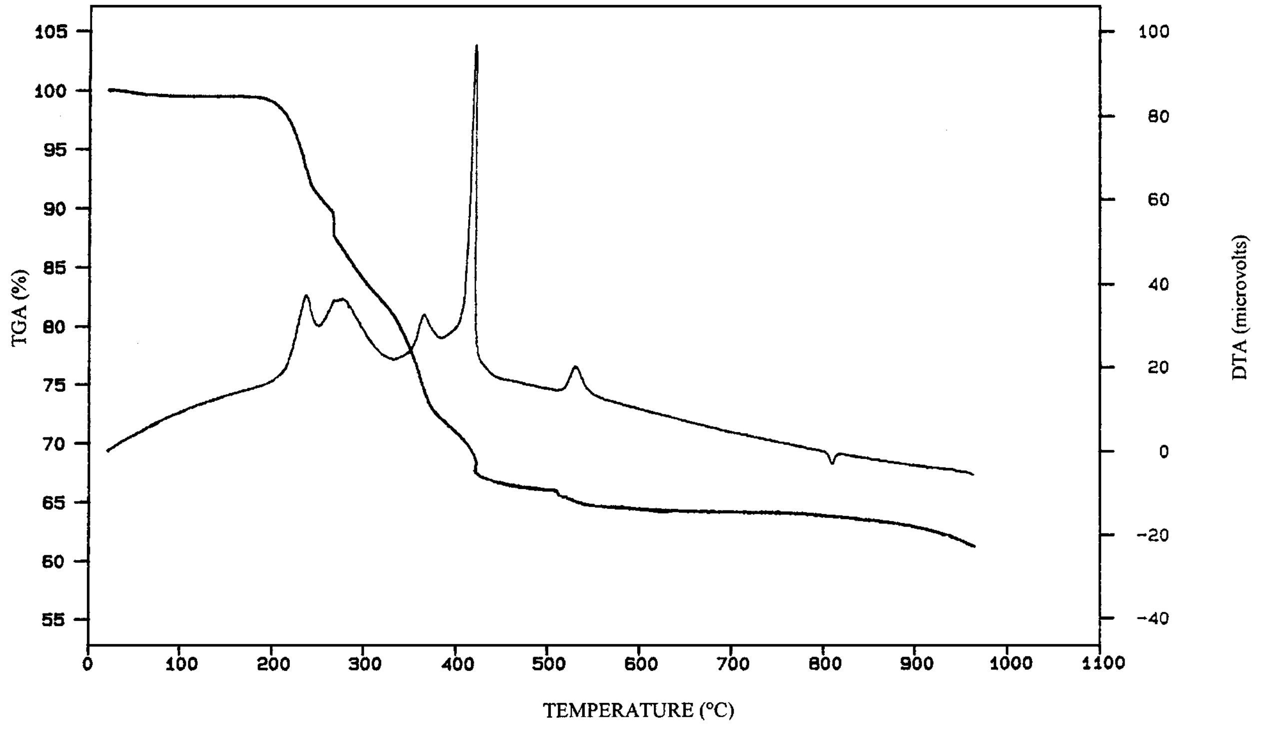

Figure 1 DTA/TGA curves for the dried precursor gel recorded in a flowing argon atmosphere. The sample weight was 14.590 mg. The heating rate was 5 °C min^{-1}.

initial negligible (~1%) weight loss below 200 °C resulting from the evaporation of adsorbed moisture. The main decomposition of the precursor occurs in the temperature range 200–500 °C, and proceeds via homogeneously distributed intermediate species, e.g., $BaCO_3$ and/or Ba, Ti oxycarbonate. It is known, that for individual barium and yttrium acetate-tartrate gels the main part of the gels decompose between 280–345 °C, and 215–365 °C, respectively [29]. Thus, the second weight loss (35%) for Ba(Y)-Ti gel can be attributed to the pyrolysis of organic compounds and species formed during the gelation process. Exothermic effects in the DTA curve are indications of these processes. A weak endothermic peak is found around 800 °C which must correspond to $BaTiO_3$ crystallization.

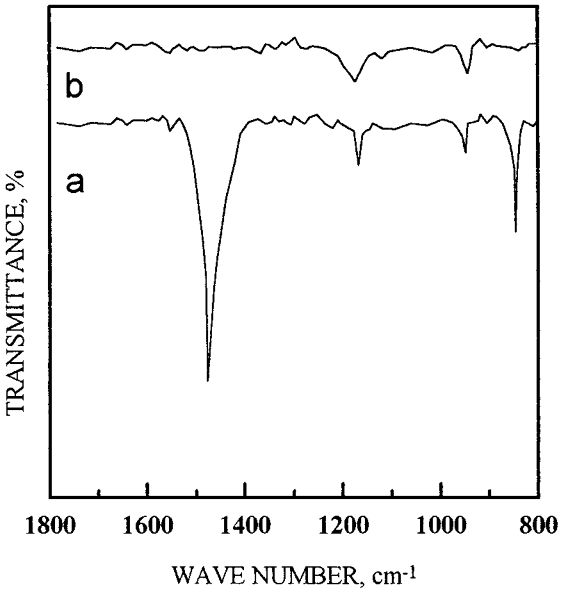

Figure 2 IR scans of the intermediate product calcined at 600 °C (a), and the final heat-treated $BaTiO_3$ powders (b).

The process of crystallization occurs, probably via the decomposition of the intermediate oxycarbonate [12, 15, 21, 27]:

$$\mathrm{Ba,Ti_{gel}} + \mathrm{air} \rightarrow \mathrm{Ba,Ti_{oxycarbonate}} + \mathrm{CO_2} \quad (1)$$

$$\mathrm{Ba,Ti_{oxycarbonate}} \rightarrow 2\mathrm{BaTiO_3} + \mathrm{CO_2} \quad (2)$$

assuming that $\mathrm{Ba,Ti_{oxycarbonate}}$ is $Ba_2Ti_2O_5CO_3$. The IR spectrum of the powder calcined at 600 °C for 2 h in static air is presumably characteristic of the intermediate $Ba_2Ti_2O_5CO_3$ phase. Fig. 2 compares fragments of the IR spectra for the intermediate product after annealing of the gel at 600 °C, and the final ceramic material, and evidently shows ionic carbonate peaks at wave number 1425 and 860 cm^{-1} for intermediate product. However, a spectrum of the synthesized barium titanate did not contain any of these peaks.

The elemental analysis of the ceramic material obtained showed that the average Ti : Ba ratio in it was 1 : 0.99(2), i.e., approximately the same as the Ti : Ba ratio found in the gel and in an intermediate 1 : 0.98(3) and 1 : 0.99(3), respectively. Hence, the calcination process does not influence the composition of the final product.

An X-ray diffraction study on the gel and intermediate isolated from the thermal decomposition of the precursor at 600 °C reveals their amorphous nature. This observation is similar to the results of Rajendran and Rao [15], where the calcination of the citrate precursor only at >650 °C results in the formation of mixed-phase (cubic and tetragonal) $BaTiO_3$. An X-ray diffraction

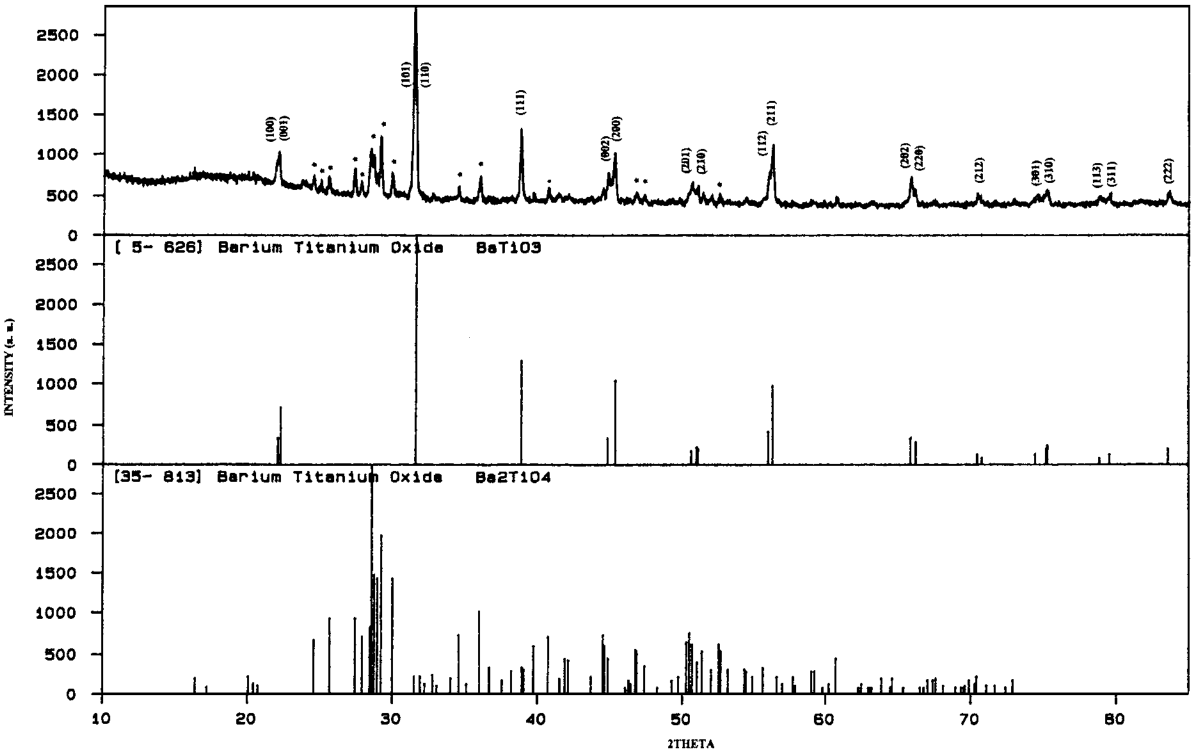

Figure 3 Powder X-ray diffraction pattern of $BaTiO_3$ synthesized by the sol-gel method. The reflections of the tetragonal $BaTiO_3$ phase are indexed. Reflections of monoclinic Ba_2TiO_4 phase are marked (∗). Entries from the Powder Diffraction File for $BaTiO_3$ (PDF No. 5 626) and for Ba_2TiO_4 (PDF No. 35 813) are shown below.

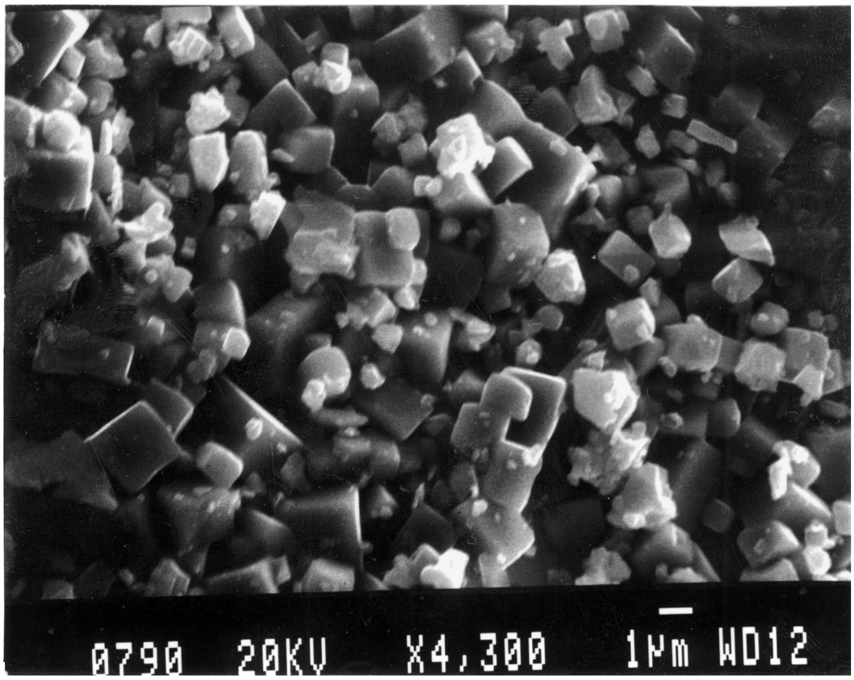

Figure 4 SEM micrograph of $BaTiO_3$ synthesized at 1300 °C. Magnification 4300×.

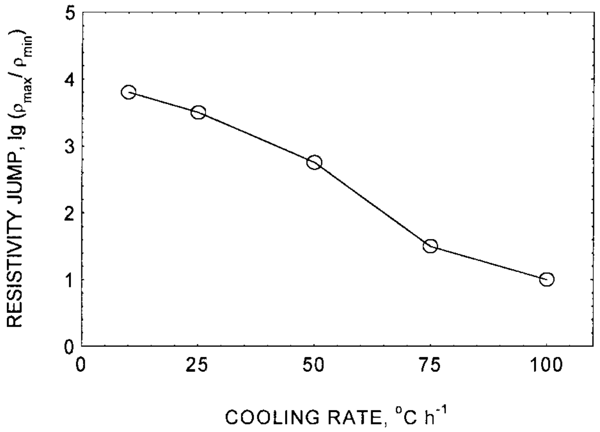

Figure 5 Resistivity jump versus cooling rate of PTCR yttrium-doped $BaTiO_3$ ceramics.

pattern of barium titanate calcined at 1300 °C is given in Fig. 3. Most of the reflections can be attributed to a tetragonal form of $BaTiO_3$. However, additional weak reflections exist in the material examined indicating the formation of the monoclinic Ba_2TiO_4 phase as well.

The textural properties of the gel precursor, intermediate and final product were investigated by SEM, from which typical morphologies were obtained. The micrograph of the gel showed that the gel is composed of aggregated 50–200 nm particles. Different sizes of the gel particles were formed, since the gelation process occured at different stages of the condensation and densification processes [36]. The powders heated at 600 °C had somewhat larger spherical particles ranging in size between 1 and 2 μm. A progressive change in morphology is evident with increased calcination temperature. Fig. 4 shows the SEM micrograph of $BaTiO_3$ obtained after calcination of the gel precursor at 1300 °C. It reveals a broad distribution of fine particles, with sizes around 1–3 μm. EDS analysis of the regular shaped crystals showed that the overall Ba : Ti ratio was very close to the nominal one (1 : 1). However, a point analysis of the small particles which can be seen around the crystals showed the Ba : Ti ratio of 2 : 1. Thus, according to EDS analysis these particles might be attributed to the monoclinic Ba_2TiO_4 phase.

The Curie point T_C of the synthesized sample was determined to be about 125 °C. However, the slope of the PTCR curve above the transition temperature and the resistivity jump depend considerably on the sample cooling rate. Fig. 5 shows the resistivity jump versus cooling rate. Evidently, the resistivity jump decreases as the cooling rate increases.

4. Conclusions

A simple aqueous sol-gel technique was investigated for synthesizing PTCR yttrium-doped $BaTiO_3$ ceramics. Homogeneous monolithic gels were achieved by complexing barium ions with tartaric acid, and using PVA as esterification agent.

According to TG and IR measurements, the formation of $BaTiO_3$ occurs probably via the decomposition of the intermediate oxycarbonate. X-ray diffraction and SEM analyses of the ceramics obtained revealed that mainly a tetragonal phase of $BaTiO_3$ was formed during calcination, but an impurity phase of monoclinic Ba_2TiO_4 was found as well. The synthesized barium titanate exhibited a PTCR effect, having a T_C at about 125 °C. The resistivity jump of the samples obtained depends on the cooling rate during high-temperature synthesis, and increased as the cooling rate decreased.

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