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Structural characterization of $BaZrO_3$ nanopowders prepared by stearic acid gel method

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Abstract

Pure barium zirconate nanopowders were successfully prepared in wet-chemistry synthesis method, using barium stearate and tetra-n-butyl zirconate as Ba, Zr sources and stearic acid as complexing reagent. The gel was calcined at 800 and 900 °C in air. Results of thermal analysis are given, including both DTG and TG. Fourier transform infrared spectrometry (FTIR), X-ray diffraction (XRD), transmission electron microscopy and (TEM) scanning electron microscopy (SEM) were used to characterize the crystallization process, the particle size and morphology of the calcined powders. The results indicated that barium zirconate nanopowders with particle size between 20 and 25 nm could be obtained after calcinations of the dried gel at 900 °C for 2 h.

Keywords: Barium Zirconate; Wet-chemistry synthesis; Nanopowders; X-ray diffraction; TEM; FTIR; SEM.

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1. Introduction

Barium zirconate of perovskite structure, $BaZrO_3$, is well known refractory material with very high melting point (2600 °C), small thermal expansion coefficient, poor thermal conductivity, good mechanical properties, *thermal* stability and low chemical reactivity towards corrosive compounds [1]. Barium zirconate is a good candidate for many structural applications such as crucible material for synthesis of barium based high-Tc superconductors, substrate for thin films deposition; thermal barrier coatings in aerospace industries and material for interface engineering of alumina fiber–alumina matrix composites [2-4]. Barium zirconate based solid solutions become ionic and/or electronic conductors and they are potential candidates for numerous types of applications in the field of electroceramics. Doped barium zirconate is known to dissolve protons in its lattice and can acts as proton conducting material in steam electrolyzers, humidity sensors and hydrogen pumps and particularly in solid oxide fuel cells (SOFC) [5–9]. A traditional method of barium zirconate synthesis consists in high-temperature solid state reaction usually between zirconia and barium carbonate preceded by powder homogenization often connected with particle size reduction. The powders prepared by such a way keep several drawbacks like a lack of reproducibility, a large particle size, wide size

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distribution, strong agglomeration and chemical in homogeneity. To overcome the processing difficulties of existing solid-state methods, "soft chemistry" methods are increasingly important in barium zirconate powder synthesis. Generally, in these methods, the powder is obtained after a low temperature decomposition of different precursors. The co-precipitation technique is a useful method for the preparation of such precursors. In this case ammonium oxalate, [10] ammonia and ammonium carbonate [11] or urea [12] were used as a precipitating agent. The organometallic compounds were also applied as barium zirconate precursors with citric acid, [13] ethylene glycol [14] or polyacrylamide15 as the complexing agent. Some other methods for barium zirconate synthesis were successfully practiced: thermal decomposition of nitrate16 or mixture of nitrate with urea as a fuel [15] in combustion mode, hydrothermal reaction [16-17] or radiation assisted synthesis [18].

In this study, we chose one typical wet-chemistry synthesis method, stearic acid gel, to try to prepare pure $BaZrO_3$ nano-powders. Stearic acid is used as the chelating agent. The carboxylic acid group and long carbon chain in stearic acid endow it with strong ability to disperse metal precursors [19]. Moreover, this synthetic process is easily controlled, save energy, resulting in less time, lead to uniform and fine powders in comparison with other methods.

2. Experimental

$BaZrO_3$ powders were prepared along a synthetic procedure as summarized in Fig. 1. Barium stearate, tetrabutyl zirconate, and stearic acid used in experiments were all of analytical grade reagents. An appropriate amount of stearic acid was first melted in a beaker at 73 °C, and then a fixed amount of barium stearate was added to the melted stearic acid and dissolved to form a green transparent solution. Next, stoichiometric tetrabutyl titanate was added to the solution, stirring to form a homogeneous light green sol, naturally cooling down to room temperature, and drying in an oven for 12 h to obtain dried gel. Finally, the gel was calcined at different temperatures in air to obtain nano-crystallites of $BaZrO_3$.

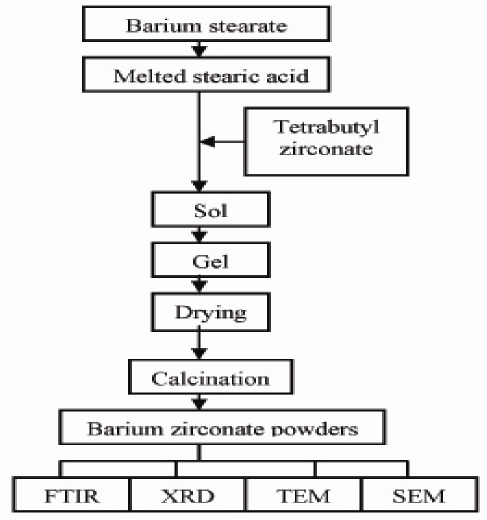

Fig.1. Flowchart for the preparation BaZrO3 of nano-powders.

The formation of process and structural characterization of $BaZrO_3$ phases have been investigated by TG/DTA, FTIR, XRD, TEM and SEM. Thermogravimetric/differential thermal analysis experiments were performed by TG/DTA (METTLER TA4000) in air to investigate the calcinations temperature and possible phase transformation from 25 to 900 °C with a heating rate of 5 °C min^{-1}.The FTIR spectrum was recorded with an MB100 (BOMEM) spectrometer by using KBr pellet. The XRD patterns of the powders were recorded on a Model PTS 3003 of

SEIFERT diffractometer using Cu Ka radiation (λ=1.5418A°) in the range from 20° to 70° (2θ) to examine the crystallization and structural development of BaZrO3 powders.

The morphology of the final products was characterized with a Philips Model EM 208 transmission electron microscope (TEM) operated at 200 kV and a scanning electron microscope (SEM) equipped with the LEO 1455 UP, OXFORD UK.

3. Results and discussion

3.1. Thermal analysis

In order to investigate the synthesis process for $BaZrO_3$, TG/DTG analysis was performed for the dried gel sample and the results are shown in Fig. 2. In Fig. 2, the sharp peak at 373.5 °C, corresponding, respectively, to a weight decrease of 70.01% was assigned to the combustion of the organic substance in the gel and the formation of $BaCO_3$ and Zr-complex (the boiling point of stearic acid is 383 °C). Another shoulder peaks, accompanied by weight loss of 20.65%, was observed from 425 to 810 °C which was assigned to the creation of $BaZrO_3$ phase. No apparent peak and significant weight loss was observed at the temperature range of over 810 °C, which indicated the minimal crystalline temperature to get $BaTiO_3$ powders by SAG was about 810 °C.

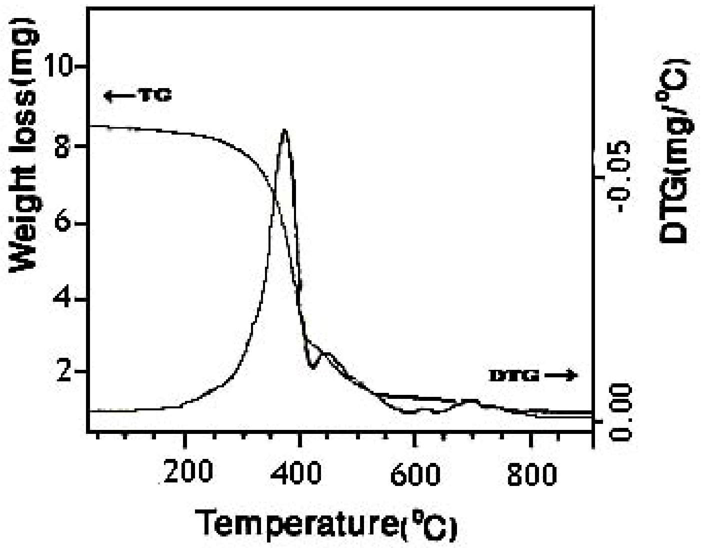

Fig. 2. TG/DTG curves of uncalcined $BaZrO_3$ dried gel.

3.2. X-ray diffraction patterns and IR spectra

Fig.3. shows the XRD patterns of the $BaZrO_3$ powders after heat-treatment from 800 to 900 °C in air for 2 h. At 800°C, the crystallization of cubic Barium zirconate phase began along with of Barium carbonate phase (*marked peaks) (Fig. 3a). Further, by increasing the calcination temperature to 900°C, the Barium carbonate phase was disappeared with an increase in the intensity of $BaZrO_3$ phase (Fig. 3b). In this temperature the nanopowders were obtained (Fig. 3b). However, at this temperature, the nanopowders displayed sharp and intense peaks indicating fine crystalline cubic $BaZrO_3$ phase. All the peaks corresponding to cubic phase were well matched with database in JCPDS (file number: 06-0399).

The formation of $BaZrO_3$ is further supported by the FTIR spectra as shown in Fig. 3. There is no evidence for the presence of any organic intermediates in the sample. All the peaks are Characteristics of the material [20] except the one at 3450 cm^{-1}, which is due to the presence of adsorbed moisture.

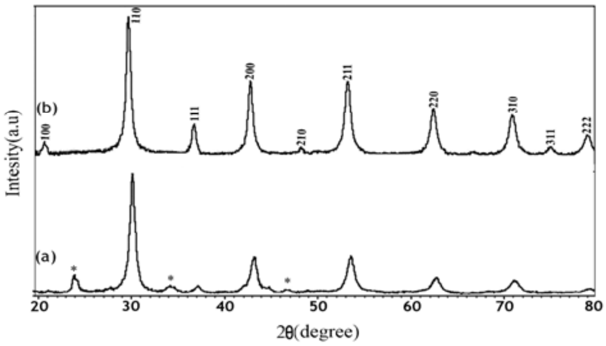

Fig. 3. X-ray diffraction patterns of $BaZrO_3$.

The small peaks around 2350 cm^{-1} observed in each sample have been attributed to atmospheric CO_2.The large vibration band observed around 539 cm^{-1} in the calcined powder is due to Zr–O vibration in the perovskite structure.

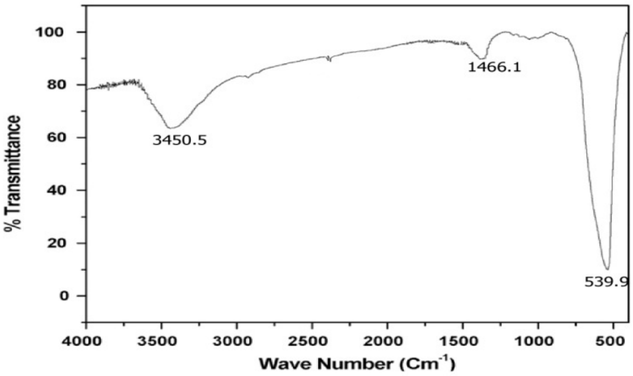

Fig. 4. FTIR spectra of the powders calcined at 900 °C.

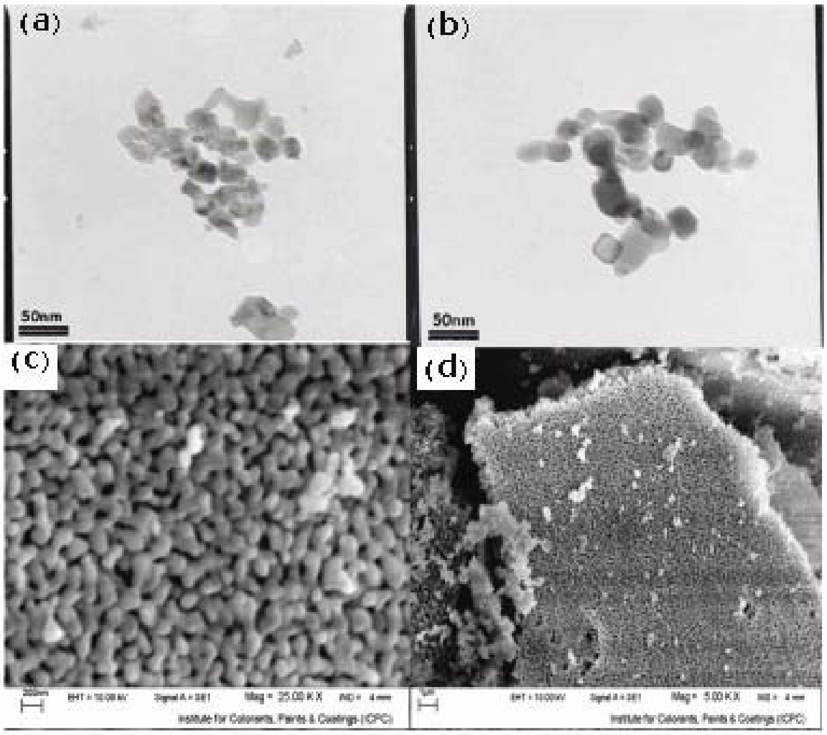

Fig. 5. TEM (a,b) and SEM (c,d) images of $BaZrO_3$ powders calcined at 900°C for 2 h.

3.3. Morphology of samples

The particle size of powders can be determined from the TEM and SEM picture. Fig. 5 is the TEM and SEM micrographs of $BaZrO_3$ powders calcined at 900 °C for 2 h. The particle size was estimated in the range of 20-25 nm. The SEM image clearly indicates the high homogeneity of the $BaZrO_3$ powders.

4. Conclusions

This study has demonstrated the feasibility of synthesis of pure $BaZrO_3$ powders using wet-chemistry synthesis route, stearic acid gel. Well crystallized $BaZrO_3$ nano-powders could be synthesized at 900 °C for 2 h. In addition, the microstructures of $BaZrO_3$ powders have been evaluated using TEM and SEM the grain sizes are shown to vary between 20 and 25 nm with high homogeneity.

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