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Preparation of ultrafine PZT powders by ultrasonic spray combustion synthesis (USCS)

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Abstract

Ultrafine PZT powders were synthesized by the ultrasonic spray combustion method from $Pb(NO_3)_2$, $ZrO(NO_3)_2{\cdot}xH_2O$, $TiO(NO_3)_2$, and CH_6N_4O precursors. The molar ratio of oxidizer and fuel was 1:1 for the maximum exothermic reaction. The DTA/TGA curves of the precursor mixture showed exothermic peaks for combustion. The external heating temperature for ultrasonic spray combustion synthesis was 800 °C. The ultrasonically generated droplets are filtered using a metal screen filter and Reynolds number was kept at a value of 1200 to avoid coagulation of droplets in the system. XRD analysis showed that the as-received powders without calcination were PZT. The lattice parameters calculated by X-ray methods were $a = b = 3.997 \pm 0.001$ Å, $c = 4.147 \pm 0.001$ Å. SEM and TEM observations showed that the particles of the synthesized tetragonal PZT powders had a 100–200 nanometer size with uniform spherical shape.

Keywords: A. Powders: chemical preparation; B. Grain size; D. PZT; E. Functional applications; Ultrafine

1. Introduction

PZT ($PbZr_{1-x}Ti_xO_3$) is an important material that is used as a dielectric and a piezoelectric [1]. Compositions close to the morphotropic phase boundary ($x = 0.52$–0.55) exhibit high dielectric constants and electromechanical coupling coefficients [2].

In general, PZT have been fabricated by solid-state reaction among the constituent oxides [3]. PZT ceramics formed by this method is heterogeneous in composition, containing compositional fluctuation [4,5]. Thus, to prepare PZT powders with homogeneous compositions, many solution techniques such as sol–gel [6], coprecipitation [7], and hydrothermal [8] methods have been developed.

However, those methods have some limitations for the synthesis of stoichiometric PZT powders. Sol–gel method [6] has difficulties such as expensive precursors, low production rate, and different hydrolysis rate among the starting materials. In coprecipitation [7] and hydrothermal method [8], due to large solubility differences among precursors, the stoichiometric composition of cations is not controllable. During calcination, the pyrolysis rates of the precursors are quite different and also the synthesized powders are agglomerated. Therefore, it is very difficult to synthesize PZT with homogeneous compositions ($x = 0.52$–0.55).

Ultrasonic spray combustion synthesis (USCS) process is basically a process using exothermic reaction of droplets which consist of oxidizers and fuels [9–15]. The exothermic combustion can cause the droplet to blow apart into smaller particles [12]. This process is known as a method which can produce multicomponent ultrafine stoichiometric particles in an atmospheric condition [12–16].

The ultrasonic spray combustion synthesis method was employed in this work to synthesize ultrafine PZT ($x = 0.52$–0.55) powders. To initiate exothermic combustion of the droplets, metal nitrates were used as oxidizers and carbohydrazide was used as a fuel source. The aerosol flow rate was controlled by use of O_2 carrier gas. And also a filter media was used to avoid the coagulation of droplets.

2. Experimental procedures

For USCS, lead nitrate ($Pb(NO_3)_2$, 99%, Aldrich Chem. Co. Inc., USA), zirconyl nitrate ($ZrO(NO_3)_2{\cdot}xH_2O$, 99.5%,

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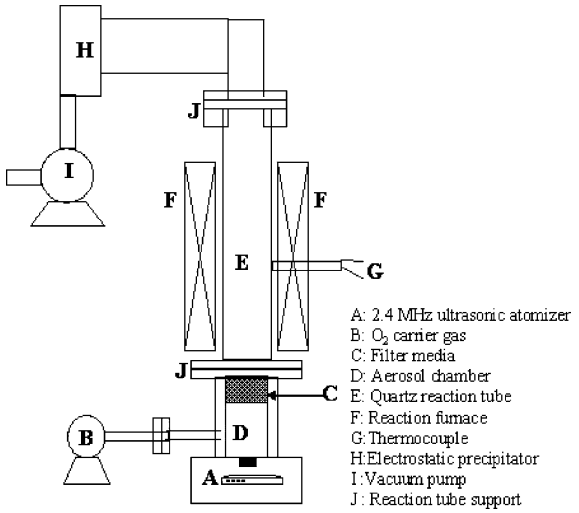

Fig. 1. Schematic diagram of the apparatus for ultrasonic spray combustion process.

Acros Organics, NJ, USA), and titanyl nitrate ($TiO(NO_3)_2$) were used as oxidizers. $TiO(NO_3)_2$ was prepared by dissolving hydrate method [17] of titanium tetrachloride ($TiCl_4$, 99.9%, Aldrich Chem. Co. Inc.). Carbohydrazide (CH_6N_4O, 97%, Acros Organics) was used as a fuel source. The stock solution for USCS was prepared by dissolving the precursors in distilled water at the molar ratio of 1:1:4:2.75. The oxidizing valency of oxidizers and fuel was 1:1 for the maximum exothermic reaction [9,18] and the concentration of the stock solution was 0.01 M. Thermogravimetric analysis (TGA) was used to study the thermal decomposition behavior of the precursors. Differential thermal analysis and thermogravimetric analysis (DTA/TGA) was used to seek for the optimal condition of ignition. Thereafter, the 0.01 M stock solution was ultrasonically sprayed into a quartz tube heated at 800 °C with O_2 carrier gas. The equipment for USCS is shown in Fig. 1. It consists of an ultrasonic atomizer, a filter media with metal screen, an external heating unit, and an electrostatic precipitator for powder collection. The frequency of the piezoelectric transducer was 2.4 MHz. The stock solution was fed at 2 ml/min. To keep a short residence time and a laminar flow [12,15], the aerosol fluid rate was maintained at 16 cm/s by using O_2 carrier gas. The synthesized particles were collected by electrostatic precipitator. The as-prepared powders were characterized by X-ray diffraction analyzer (XRD, Philips, PW 3710, Holland), and transmission electron micrographs (TEM, Philips, Technai 20, Holland).

3. Results and discussion

The weight loss behavior of the precursors of lead nitrate, zirconyl nitrate, titanyl nitrate (oxidizer), and carbohydrazide (fuel) were quite different from each other during heating. Lead nitrate was decomposed from 330 to 800 °C. In general, metal anhydrous nitrates have their own crystallinities and the decomposition of them starts around their melting temperature. The melting temperature of lead nitrate is 470 °C. Thus, almost decomposition was observed between 450 and 535 °C. Zirconyl nitrate was decomposed from 100 to 400 °C. The decomposition of titanyl nitrate finished below 250 °C. Carbohydrazide was decomposed between 170 and 350 °C.

The thermal weight loss behavior of precursors was quite different. Thus, the heating schedule of the USCS should be carefully controlled to initiate ignition of droplets. The DTA/TGA analysis of the precursor mixture, in Fig. 2, showed exothermic peaks at 214 and 350 °C. The exothermic peaks might be considered as an evidence of ignition and burning in the system. The thermal decomposition

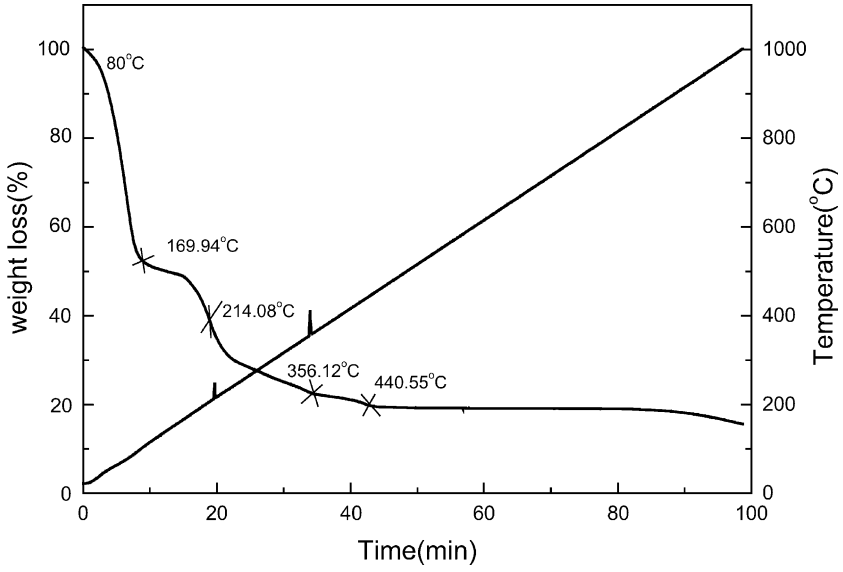

Fig. 2. DTA/TGA result of precursor mixture.

process gives a series of different reactions in which intermediate products are formed in one step and destroyed in succeeding steps (chain reaction) [12–14]. The intermediate products issued by the mixture are known as chain carriers since they help carry the reaction to combustion. Energy chain, in particular, depends on the energy rich molecule retaining its energy, which is not lost either by radiation or collision with other types of molecules, until it is used in the particular type of collision that propagates the chain. The formation of collision complexes and the stability of polyatomic molecules with a large amount of internal energy are also of importance in determining the kinetics of the combustion process [11–14,19].

The exothermic peaks of the precursor mixture were, however, too small to complete phase transition of the synthesized product. In case of USCS, the combustion reaction is limited to a droplet. The amount of equilibrium species decomposed from droplets is not enough to initiate ignition, and also H_2O contents and residence time are severely affected. Thus, combustion reaction may not be complete. Therefore, sufficient heat should be supplied onto droplets from external heating source during the combustion process to avoid incomplete reaction.

Heating schedule of the droplets in ultrasonic spray combustion method should be carefully controlled by the results from DTA/TGA analysis, and therefore short residence time in the reactor is needed to satisfy the appropriate heating schedule during combustion synthesis. Thus, to initiate ignition of droplets the furnace temperature as an external heating source was chosen at 800 °C in this study. The sprayed droplets pass through the 40 cm height of the reactor maintained at 800 °C within 2.5 s for this experiment. To avoid coagulation of droplets [19], a metal screen filter was used to lower the ultrasonically generated droplet number concentration and to get rid of large droplets. Hot air with laminar flow was introduced into the reactor to avoid condensation of droplets within the aerosol generating chamber. After that, the precursor solution was ultrasonically sprayed into the reaction chamber at 800 °C for USCS. To maintain laminar flow in the system O_2 carrier gas was introduced into the reactor. To achieve laminar flow [12], the Reynolds number was kept at a value of 1200.

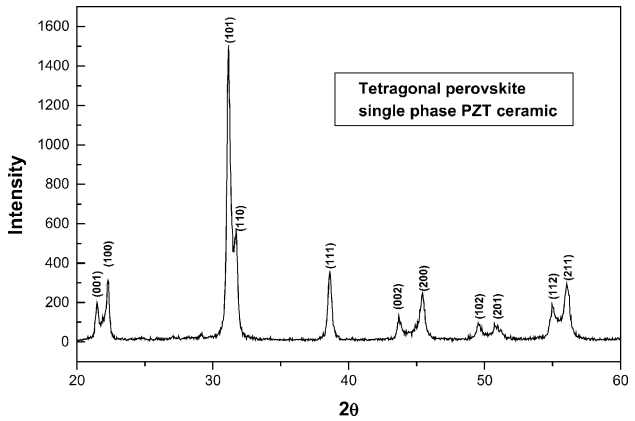

Fig. 3. X-ray diffraction patterns of the as-received product by ultrasonic spray combustion method with 0.01 M stock solution.

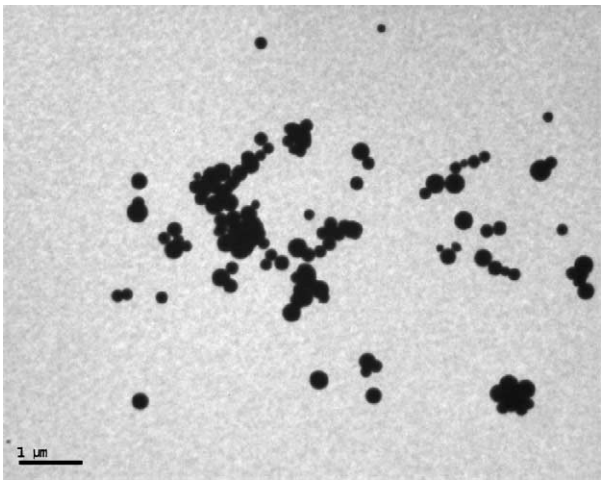

Fig. 4. Morphology of PZT particles from TEM observation.

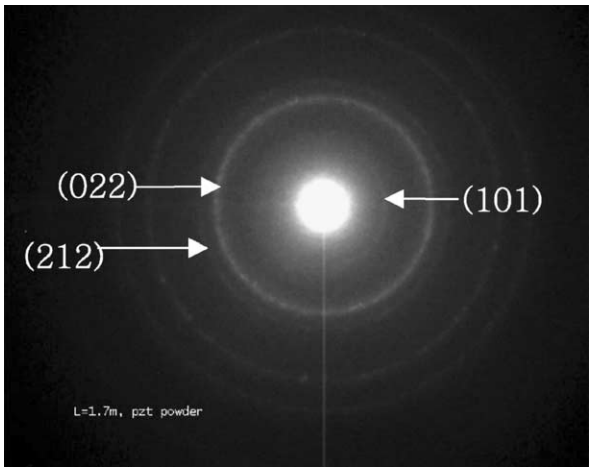

Fig. 5. TEM diffraction pattern of PZT.

X-ray diffraction patterns, in Fig. 3, showed that the synthesized product was fully crystalline PZT perovskite structure. The lattice constants calculated from XRD patterns were $a = b = 3.997 \pm 0.001$ °C and $c = 4.147 \pm 0.001$ °C. The results were close to the result which has been reported by Kakegawa [5].

TEM observations, in Fig. 4, showed that the particle size was 100–200 nanometer, and the morphology of the particles was an uniform spherical shape. Also, TEM diffraction pattern of the particles in Fig. 5 indicated that the nanometer particles were tetragonal PZT.

4. Summary

Ultrafine PZT powders were synthesized by ultrasonic spray combustion synthesis (USCS). To complete

combustion of the droplets, $Pb(NO_3)_2$, $ZrO(NO_3)_2{\cdot}xH_2O$, $TiO(NO_3)_2$, and CH_6N_4O with the molar ratio 1:1:4:2.75 were mixed in the distilled water. The heating schedule of the droplets in USCS method was carefully set-up by the results from DTA/TGA analysis and by the consideration of droplet size. The external heating temperature for ultrasonic spray combustion synthesis was 800 °C to supply sufficient external energy. The ultrasonically generated droplets are filtered using a metal screen filter to avoid coagulation of droplets in the system. To achieve laminar flow, the Reynolds number was kept at a value of 1200. The particles of the synthesized PZT powders had a 100–200 nanometer size with an uniform spherical shape. XRD and TEM diffraction patterns showed that the synthesized product were fully crystalline tetragonal PZT phase.

Acknowledgements

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