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Synthesis of submicron $PbTiO_3$ particles by the water-in-oil emulsion process

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Abstract

Submicron $PbTiO_3$ powder with spherical morphology was successfully synthesized by the water-in-oil emulsion process. The aqueous solution containing lead and titanium cations was well emulsified in *n*-octane solution by adding appropriate surfactant. During the heating of the dried precursors, tetragonal $PbTiO_3$ began to form from above 560°C. Heating at 900°C without soaking yielded pure $PbTiO_3$. The particle size of the obtained $PbTiO_3$ was within the submicron range, and considerably smaller than that prepared by the conventional solid-state reaction route. Agitation time in the emulsification process was found to significantly affect the morphology of $PbTiO_3$ powder. Insufficient agitation time resulted in the non-uniform distribution of particle size.

Keywords: Synthesis; $PbTiO_3$; Submicron; Particles; Emulsion; Microstructure

1. Introduction

The properties of ceramics are greatly affected by the characteristics of the powder, such as particle size, morphology, purity, and chemical composition. Using solution processes, e.g. coprecipitation, sol–gel process, and hydrothermal process, instead of a solid-state mixing process has been confirmed to efficiently control the morphology and chemical composition of synthesized powder. Recently, the emulsion process has been found to be the other promising solution process in the synthesis of fine ceramic powders having a narrow size distribution [1]. Several researchers have utilized this technique to prepare single and multi-component ceramic powder [2–7]. The basic concept of the emulsion process is to disperse a solution containing the desirable species in an immiscible liquid. Through adding an appropriate surfactant and using emulsifying treatment, the solution having the desirable components can be well dispersed to form tiny liquid droplets in the immiscible liquid. Since each droplet acts as an independent reactor, the morphology of the powder can be easily controlled by the droplet size.

The purpose of this study was to utilize the emulsion process in w/o (water in oil) system to prepare submicron $PbTiO_3$ powder. To simplify the synthesis process, the $PbTiO_3$ precursors were obtained by directly drying the emulsion solution without adding any precipitant. The crystalline variation and microstructural evolution during the formation process were investigated. Furthermore, the effects

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of emulsifying time on the characteristics of PbTiO$_3$ powder were also examined.

2. Experimental

The preparation of the aqueous titanium ion solution was similar to Yamamura's method [8]. TiCl$_4$ was dissolved into cold de-ionized water surrounded by an ice bath. Ammonia was added in the solution to precipitate titanium ions. After the precipitates were filtered and washed by de-ionized water repeatedly to remove chlorine ion, the precipitates were dissolved in HNO$_3$ solution to obtain TiO(NO)$_3$ solution. Then Pb(NO)$_3$ was added into titanium ion solution at a molar ratio of $Pb^{2+} : Ti^{4+} = 1 : 1$ to obtain the aqueous phase. On the other hand, *n*-octane was chosen for preparation of the oil-phase. For stabilizing the water-in-oil (w/o) emulsions, 1 wt% of surfactant (Span-80 (Nacalai Tesque, Inc. Japan)) was added into *n*-octane. After the aqueous phase and the oil phase were prepared, these two phases, mixed at a volume ratio of 3 : 1, were continuously agitated by a homogenizer at 500 rpm for 30 or 70 min for obtaining homogeneous emulsions. Drying was followed to remove the solvents, and then the species present in the emulsions became PbTiO$_3$ precursors in solid form.

Differential thermal analysis (DTA) and thermogravimetry analysis (TGA) were conducted at a rate of 10°C/min to detect thermal variations and weight change of the resulting precursors during the heating process. X-ray powder diffraction (XRD) was utilized to identify the compounds present in heat-treated specimens. Scanning electron microscopy (SEM) was used to examine the microstructural evolution and particle size of the specimens.

3. Results and discussion

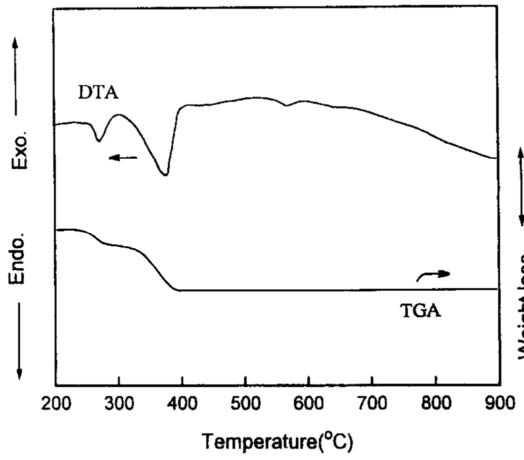

Fig. 1. Differential thermal and thermogravimetry analysis of PbTiO$_3$ precursors prepared via the emulsion process by agitation for 70 min.

Fig. 1 shows the DTA and TGA results for PbTiO$_3$ precursors prepared by agitating the aqueous and oil phases for 70 min. The endothermic peaks appearing at around 270 and 380°C were attributed to the evaporation of residual organic species. These endothermic reactions were associated with a weight loss of around 4.1%. On further heating, an endothermic peak was found at 560°C. No other thermal anomaly appeared at elevated temperatures up to 900°C. For realizing the formation process, PbTiO$_3$ precursors were quenched from different temperatures and then analyzed by XRD. Representative XRD patterns for quenched specimens are plotted in Fig. 2. At 500°C PbO and a trivial amount of PbTiO$_3$ with undeveloped crystal structure were identified. An unknown phase having a diffraction peak at

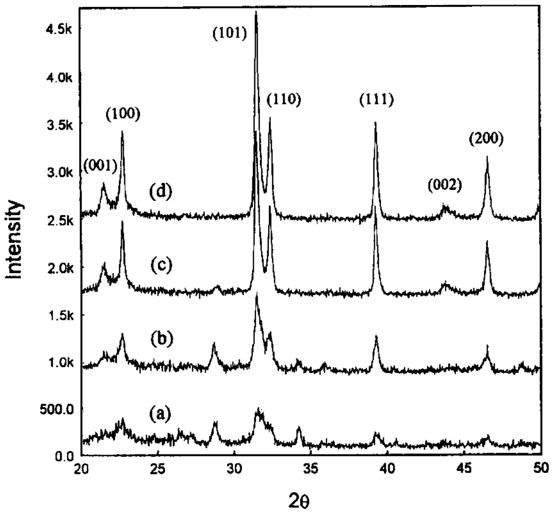

Fig. 2. X-ray diffraction patterns of PbTiO$_3$ precursors quenched at (a) 500°C, (b) 600°C, (c) 800°C, and (d) 900°C.

$2\theta = 34°$ was also found. After heating at 600°C the amount of $PbTiO_3$ was increased, and the crystal structure became well-developed. From the appearance of the diffraction peaks corresponding to (001), (100), (101), (110), (002), and (200) planes, the formed $PbTiO_3$ was confirmed to exhibit the tetragonal structure. The tetragonal phase gradually evolved with increasing temperature. Heating up to 900°C without soaking resulted in pure $PbTiO_3$ without any residual compounds. According to the results shown in Fig. 1 and 2, the endothermic reaction at 560°C was confirmed to be the formation reaction of $PbTiO_3$.

To reduce the formation temperature for pure $PbTiO_3$, isothermal calcination for 2 h ranging from 500 to 900°C was conducted. After calcination at 500°C, PbO and a small amount of $PbTiO_3$ were formed in the specimens. At 600°C the amount of PbO decreased. After 700°C calcination, pure $PbTiO_3$ formed. At 900°C the crystal structure of $PbTiO_3$ was developed further. The crystallization behavior of $PbTiO_3$ was similar to that of $PbTiO_3$ prepared by the coprecipitation process. The complete crystallization of $PbTiO_3$ precipitates required calcination at temperatures higher than 800°C [9].

The microstructure of quenched and calcined specimens was observed via SEM. Below 600°C no specific morphology could be found in the specimens; however, above 600°C the quenched specimens exhibited particulate morphology, indicating the formation of $PbTiO_3$. The microstructure of the specimen quenched at 700°C showed that the particle size of $PbTiO_3$ was around 0.1 to 0.2 μm (see Fig. 3a). After calcination at 900°C, $PbTiO_3$ particles became coarsened, and the particle size was increased to be 0.2 to 0.4 μm (see Fig. 3b). In the quenched and calcined specimens, $PbTiO_3$ particles exhibited spherical morphology with a narrow size distribution. The EDS analysis was performed to examine the chemical composition of $PbTiO_3$ powder. The results indicated that the molar ratio of lead to titanium was approximately unity. Compared with the precipitation process [10], the emulsion process was easier in terms of controlling the stoichiometry of $PbTiO_3$ powder for preparing the pure compound.

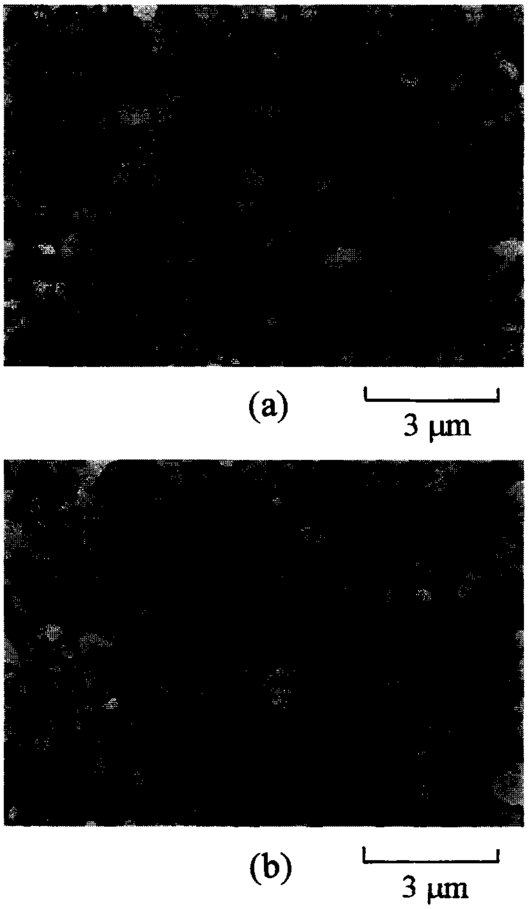

Fig. 3. Scanning electron micrographs of $PbTiO_3$ emulsion precursors prepared by agitation for 70 min. (a) Powder quenched at 700°C, and (b) powder calcined at 900°C for 2 h.

The effects of agitation time of aqueous and oil phases on the obtained $PbTiO_3$ precursors and powder were further investigated. The agitation time during emulsion formation was shortened to 30 min. The other procedures were the same as described in Section 2. The DTA and TGA results for this precursor were similar to those shown in Fig. 1. An endothermic reaction was also found at around 560°C at which the $PbTiO_3$ phase started to form. After 900°C calcination for 2 h, pure $PbTiO_3$ powder was obtained. However its morphology was different from that obtained after 70 min agitation as shown in Fig. 3b. The microstructure of the obtained $PbTiO_3$ powder is shown in Fig. 4a. This figure reveals that the $PbTiO_3$ powder exhibited a non-homogeneous size distribution, with small particles (0.2 to 0.4 μm) and large particles (0.8 to 2.0 μm). These results imply that the variation in agitation time did not influence

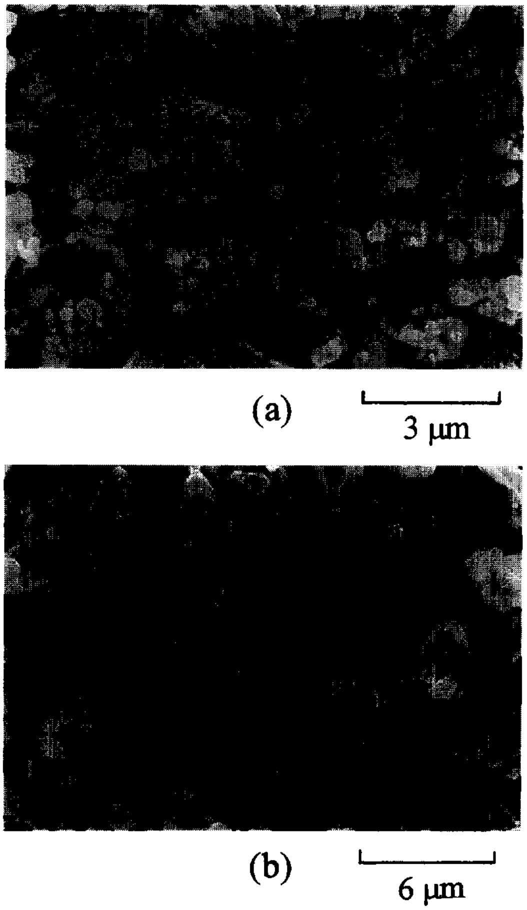

Fig. 4. Scanning electron micrographs of 900°C-calcined $PbTiO_3$ precursors prepared via the (a) emulsion process by agitating for 30 min, and (b) solid-state reaction process.

the $PbTiO_3$ formation process; however, it did affect the morphology of $PbTiO_3$ powder. It is considered that the insufficient agitation time, namely, insufficient mechanical force could not evenly disperse the aqueous solution in the oil phase. In addition, the formed droplets might coalesce to yield larger droplets due to insufficient covering of the surfactant on the droplets. As a result, emulsion droplets with different size were formed during the short agitation period resulting in the non-homogeneous size distribution of $PbTiO_3$ powder. Apparently, the emulsification process is critical for tailoring the size distribution of $PbTiO_3$ powder. The microstructure of $PbTiO_3$ powder prepared by solid-state reaction after calcination at 900°C for 2 h is shown in Fig. 4b. The shape of $PbTiO_3$ grains was faceted, and the particle size ranged from 1.8 to 5.6 μm. Comparing the $PbTiO_3$ prepared by the emulsion technique and that prepared via a solid-state reaction, it is obvious that the emulsion process can significantly reduce the particle size and results in a narrow size distribution. It is suggested that the emulsion process may allow effective control of the particle size and particle morphology in the synthesis of other complex-cation oxides.

4. Conclusion

(i) $PbTiO_3$ powder was successfully synthesized by the w/o emulsion technique in which the aqueous solution containing lead and titanium cations was emulsified in *n*-octane oil-phase.

(ii) When heating the obtained precursors, $PbTiO_3$ with a tetragonal structure began to form from above 560°C. Heating at 900°C without soaking yielded pure $PbTiO_3$. The particle size obtained $PbTiO_3$ was within the submicron range. The particle size was much smaller than that obtained by the conventional solid-state process.

(iii) The agitation time for the emulsification process was found to significantly affect the morphology of the obtained powder. Insufficient agitation time resulted in a non-uniform size distribution of particle size.

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