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Full Length Article

Synthesis of highly disperse tetragonal $BaTiO_3$ nanoparticles with core–shell by a hydrothermal method

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ABSTRACT

In order to synthesize of high-dispersion and tetragonal $BaTiO_3$ (BT) nanoparticle, a hydrothermal method is used in a mixture of chloride metal sources and KOH with polyvinylpyrrolidone (PVP). The properties of BT–PVPs prepared by different reaction temperature and time are investigated via XRD, FE-SEM, DLS, FT-IR, and TEM to clarify the changes of the crystal phase, dispersion, and particle structure. The reaction is finished at 230 °C for 24 h and the critical reaction condition for that the crystal phase of the obtained BT particle changed from the cubic to the tetragonal is found to be 190 °C fixed in reaction time 24 h, and 9 h. During reaction the PVP on the BT surface decomposed to different form, and the PVP plays the role of dispersant in aqueous solution. By the hydrothermal condition of 230 °C for 24 h almost monodisperse BT–PVP with sizes of 83 nm and tetragonality (c/a) of 1.0062 were synthesized. The structure of nanoparticle, core (BT)–shell (PVP) was investigated by FT-IR and direct observed by TEM and the mechanism of particle growth and dispersion was discussed.

1. Introduction

$BaTiO_3$ (BT) is a well-known material because of its ferroelectric [1–3] and piezoelectric [4–6] properties. It is mainly used in multilayer ceramic capacitors (MLCCs), piezoelectric transducers, and other electronic applications. Recently, the size of the dielectric layers of MLCCs has been reduced to 0.5 μm with the market requirement of the miniaturization of electronic devices. In order to retain the high capacitance of MLCCs, highly disperse tetragonal BT powders with particle sizes below 100 nm can be used for their manufacture.

Generally, tetragonal BT is synthesized by a solid-phase method which involves high temperature sintering, but the corresponding manufacturing procedure is very expensive. In contrast, hydrothermal method can be easily used to prepare tetragonal BT with sizes below 100 nm and narrow size distributions [7–10] at much lower reaction temperatures. However, one of the drawbacks of this technique is the formation of OH lattice defects in aqueous reaction solutions, which reduce the MLCC capacitance and ultimately deteriorate the device quality. Adam et al. [11] proposed the use of a solvothermal method instead of the hydrothermal one for the preparation of smaller and defect-less BT nanoparticles, in which aqueous solution are replaced with organic solvents. Similar studies were conducted by Kwon et al. [12], Habib et al. [13].

Many techniques for the synthesis and growth of relatively large BT particles have been discussed [9,10]. However, as the particle size decreased to the nanoscale, particle aggregation became a significant problem. Very few research studies about polyvinypyrrolidone (PVP) was utilized as a dispersant for BT nanoparticles, although PVP has been widely used in the synthesis of metal and other metal oxide nanoparticles as a stabilizer, template, and inhibitor of particle growth. In a previous study, we have reported the synthesis of highly disperse BT–PVP nanoparticles at temperature below 100 °C and atmospheric pressure that PVP served as a stabilizer and inhibitor [14], through adsorbed on the BT surface via hydrogen bonding [15]. The dispersion of the synthesized nanoparticles was achieved via the PVP steric effect; however, the phase of the BT–PVP obtained at low temperatures was cubic. In order to synthesize highly disperse tetragonal BT nanoparticles with core–shell structure in one step, a new PVP-assisted hydrothermal method has been developed as shown in

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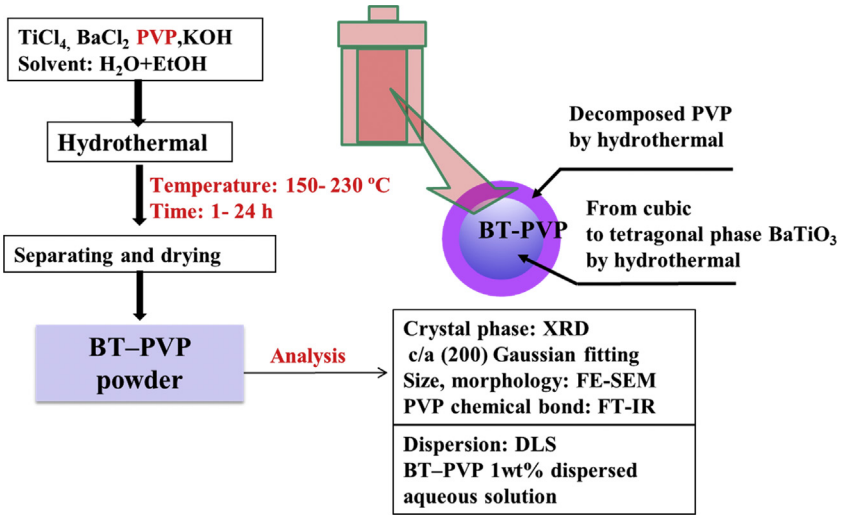

Fig. 1. Schematic flow of hydrothermal process and analysis $BaTiO_3$–PVP (BT–PVP) on core oxide particle and surface adsorbed PVP.

Fig. 1. The PVP was put into the reaction vessel with other raw materials, and set into the autoclave. It is necessary to investigate the change of PVP structure and dispersion with the reaction conditions of temperature and time because it maybe decompose at high temperature and pressure. The change of crystal phase of BT during the hydrothermal reaction with the PVP is also to studied.

In order to clarify these issues, we have studied the structure of BT–PVP by X-ray diffraction (XRD), Field emission scanning electron microscopy (FE-SEM), Fourier transform infrared spectroscopy (FT-IR), Transmission electron microscopy (TEM) and so on. And the mechanism of the particle growth and the dispersion is discussed.

2. Experimental procedure

2.1. Materials

Titanium tetrachloride ($TiCl_4$, 90+), and barium chloride dehydrate ($BaCl_2{\cdot}2H_2O$, 90%) precursors as well as potassium hydroxide (KOH, 85%) mineral agent were purchased from Wako Pure Chemical Industries Ltd., Japan. PVP dispersant with a molecular weight of 10,000 g/mol was obtained from Sigama–Aldrich Com. USA.

2.2. Synthesis of $BaTiO_3$–PVP nanoparticles

Fig. 1 shows the schematic flow of synthesis and analysis of BT–PVP. The inset is the images of reaction vessel including a 50 mL Teflon container and an autoclave. First, aqueous solution containing 0.32 M of $BaCl_2{\cdot}2H_2O$, 0.2 M of $TiCl_4$, 100 g/L of PVP, and 2.3 M of KOH were mixed in the 50 mL Teflon container under constant stirring. The reaction solution with a total volume equal to about 40 vol.% of the 50-mL Teflon container was prepared by mixing distilled water and ethanol (EtOH) at a volume ratio of 3:1. The resulting mixture was sealed and placed into the autoclave and heated at specified reaction temperature and time. After the reaction, the container was cooled to room temperature and the resulting white precipitates was extracted by centrifugation. The precipitate was first washed with distilled water and ethanol, and then dried at 60 °C for 24 h to obtain BT–PVP particles. The detailed reaction conditions utilized in this study are summarized in Table 1.

2.3. Characterization

The crystalline phase of the obtained BT particles was examined by X-ray diffraction (XRD, Smartlab Rigaku Corp. Cu Kα 1.5405 Å, 30 mA/40 KV, scan speed 20°/min, range of 2θ around 10–90°). In order to accurately evaluate the tetragonality of BT–PVP particle, the peak of (200) plane was measured again in 0.01°/min scan speed around 44–46°. And it was fitted by the Gaussian function using Microcal Origin program to deconvolute into two peak of (200) and (002) plane and calculate the **c** and **a** lattice parameters as Kwon et al. reported [12]. The tetragonality of the produced BT–PVP nanoparticles was quantified by the value of **c/a**. Particle morphology was observed via field emission scanning electron microscopy (FE-SEM, JSM-6335FM, JEOL Ltd.), and transmission electron microscopy (TEM, JEM-1000 K, JEOL Ltd.). The sizes and size distributions of BT–PVP particles were determined via image analysis performed by using the specialized SmileView software. Dynamic light scattering analysis (DLS, FPAR-10001, Otsuka Electronics Co., Ltd.) was used to evaluate the dispersibility of 1 wt.% BT–PVP in aqueous solutions by conducting five sequential measurements. The amount of the PVP dispersant adsorbed on the BT surface was evaluated via thermogravimetry–differential analysis (TG-DTA, 2010SA, Bruker AXS K.K., Japan). Zeta potentials of the synthesized BT–PVP nanoparticles in aqueous solution were measured by electrophoretic light scattering (ELS-Z1/Z2, Ostuka Electronics Co., Ltd., Japan). The chemical structure of PVP dispersant molecules adsorbed on the BT surface was determined by FT-IR (FT/IR-610, JASCO).

Table 1
Reaction condition utilized during the BT–PVP synthesis in this study.

Parameter	Reaction temperature (°C)	Reaction time (h)	PVP concentration (g/L)
Reaction temperature	150, 170, 190, 210, 230	24	100
Reaction time	230	1, 5, 9, 21, 24	100

3. Results and discussion

3.1. Effect of reaction temperature and time on particle growth of $BaTiO_3$–PVP

Tetragonal BT can be easily prepared at 240 °C by the hydrothermal method described by Xu et al. [16]. In addition, Kwon et al. [12] reported that the present of several percent of EtOH in reaction solution could significantly improve the tetragonality of the produced BT nanoparticles. Hence, in order to prepare highly disperse tetragonal BT, EtOH and PVP were added to the reaction mixture

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