



Full Length Article

Effect of PVP on the synthesis of high-dispersion core-shell barium-titanate-polyvinylpyrrolidone nanoparticles

Q1 Jinhui Li^{a,c}, Koji Inukai^b, Yosuke Takahashi^b, Akihiro Tsuruta^c, Woosuck Shin^{a,c,*}Q2 ^a Department of Frontier Materials, Nagoya Institute of Technology, Nagoya 466-8555, Japan^b R&D Center, Noritake Co., Ltd., Miyoshi 470-0293, Japan^c Electroceramics Research Group, AIST, Nagoya 463-8560, Japan

ARTICLE INFO

Article history:

Received 4 March 2017

Received in revised form 1 May 2017

Accepted 1 May 2017

Available online xxx

Keywords:

BaTiO₃

Nanoparticle dispersion

Polyvinylpyrrolidone

ABSTRACT

Monodispersed nanoparticles consisting of barium titanate (BaTiO₃, BT) as the core and polyvinylpyrrolidone (PVP) as the shell were synthesized in a PVP-assisted low-temperature process in an aqueous solution at ambient pressure. In order to clarify the mechanism of this unique BT-PVP nanoparticle growth and the origin of the dispersion, the concentration and molecular weight of PVP used in the synthesis were varied, and the size and dispersion of the resulting nanoparticles in water were investigated by field-emission scanning electron microscopy and dynamic light scattering. Monodispersed nanoparticles with an average size of 130 nm were obtained by using an intermediate PVP concentration of 100 g/L and a PVP molecular weight of 10,000 g/mol. The thickness of the PVP shell was estimated by thermogravimetric analysis. For the highly dispersed BT-PVP, the thickness of PVP adsorbed on the BT surface was around 3–5 nm. Direct SEM observation of monodispersed BT-PVP in an aqueous solution using a unique sample holder was also demonstrated for the first time.

© 2017 The Ceramic Society of Japan and the Korean Ceramic Society. Production and hosting by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Barium titanate (BT, BaTiO₃) is a ferroelectric compound with a perovskite structure. It is an important ferroelectric ceramic material that is mainly used in multilayered ceramic capacitors, semiconductors, positive temperature coefficient (PTC) thermistors, and piezoelectric devices [1–6]. In recent years, the increasing trend for miniaturization in the electronics industry has created a strong demand for nanometer-sized BT particles with spherical shape, low sintering temperature accompanied by a high sintering density, and high dielectric constant accompanied by a low dissipation factor.

BT particles are commonly produced by either a high-temperature solid-state process [7–9] or a wet chemical process [10,11]. Compared to the solid-state process, the wet chemical process can produce BT particles with higher purity and smaller size at

lower temperature. There are many approaches to the wet chemical process, such as sol-gel [12], co-precipitation [13], and hydrothermal [14] techniques. In particular, low-temperature (below 100 °C) synthesis of BT in aqueous systems has attracted much attention because of its simplicity, cost effectiveness, and suitability for industrial-scale production. The low-temperature synthesis of BT can be carried out mainly by two methods: direct synthesis at atmospheric pressure, as reported by Wadda et al. [15], and hydrothermal synthesis [16]. To date, the minimum particle size of BT can be controlled to reach tens of nanometers.

Polyvinylpyrrolidone (PVP) is used extensively in the synthesis of nanoparticles as a stabilizer [17], molding agent [18], or reducing agent [19]. It is an amphiphilic polymer that has an alkyl hydrophobic side group and a hydrophilic pyrrolidone group. It is easily soluble in water and many organic solvents because of the formation of hydrogen bonds between the carbonyl group (C=O) in PVP and the solvent.

Our group successfully synthesized BT via a PVP-assisted low-temperature process [20], which is a simple method that can overcome the problems of particle size and aggregation in a single step. Recently, we investigated the effect of precursor concentration, reaction temperature and time, and KOH concentration on the particle size of BT. Our results indicated that the KOH concentration was a key factor that not only affected the particle size, but also the

Abbreviations: BT, barium titanate; DLS, dynamic light scattering; PVP, polyvinylpyrrolidone; FE-SEM, field-emission scanning electron microscopy; IEP, isoelectric point; NVP, N-vinylpyrrolidone; TG, thermogravimetry; XRD, X-ray diffraction.

Q3 * Corresponding author at: Department of Frontier Materials, Nagoya Institute of Technology, Nagoya 466-8555, Japan. Fax: +81 52 736 7244.
E-mail address: w.shin@aist.go.jp (W. Shin).

<http://dx.doi.org/10.1016/j.jascer.2017.05.001>

2187-0764/© 2017 The Ceramic Society of Japan and the Korean Ceramic Society. Production and hosting by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Table 1
Reaction conditions and results of BT–PVP synthesis using solutions with different PVP concentrations. The molecular weight of PVP was 10,000 g/mol.

Sample	PVP concentration (g/L)	Crystallite size ^a (nm)	Lattice parameter (Å)	Particle size ^b (nm)	Shell thickness ^c (nm)
BT-C1	0	48.7	4.0404	205	0
BT-C2	25	49.0	4.0401	191	2.0
BT-C3	50	44.5	4.0428	141	4.8
BT-C4	100	43.3	4.0408	130	2.8
BT-C5	200	40.1	4.0409	120	2.6
BT-C6	300	39.2	4.0405	102	3.6
BT-C7	350	51.8	4.0399	116	6.5
BT-C8	450	50.7	4.0423	97	7.7

^a Calculated using Scherrer's equation.^b Measured by FE-SEM.^c Calculated using Eq. (2) in this paper.

adhesion of PVP on the BT surface and the dispersion of BT in an aqueous solution. However, the investigation was inconclusive in terms of the role of PVP in the particle growth and the dispersion mechanism.

In this study, we investigated the effects of concentration and molecular weight of PVP on the growth of crystallites and particles of BT–PVP during its synthesis and the BT–PVP re-dispersion in an aqueous solution. The thickness of the PVP film adsorbed on the BT surface was estimated quantitatively, and the morphology of the adsorbed PVP was examined. Using a new type of sample holder for SEM measurements and the same method demonstrated by Izu et al. [21], the dispersed particles of BT–PVP in an aqueous solution were directly observed for the first time.

2. Experimental method

2.1. Preparation of BaTiO₃–PVP nanoparticles

Nanoparticles of BT–PVP were prepared according to previously reported procedures [20]. The precursor concentration of TiCl₄ and BaCl₂ were 0.2 M, and the concentration of KOH was 1.8 M. The reaction temperature was 80 °C and the reaction duration was 1 h. In order to investigate the effect of PVP in this reaction solution, the concentration of PVP with molecular weight of 10,000 g/mol was varied from 0 to 450 g/L. The molecular weight of PVP was then varied from 2500 to 360,000 g/mol while the concentration was kept constant at 50 g/L. PVP is formed by polymerizing the *N*-vinylpyrrolidone (NVP) unit, and the molecular weight of each unit of NVP is 111 g/mol. The number of units of NVP in different molecular weights was calculated, and the length of each PVP was calculated using Eq. (1) [22]:

$$L_{\max} = \left(\frac{2}{3}\right)^{\frac{1}{2}} nl, \quad (1)$$

where L_{\max} is the length of the PVP polymer, n is the number of monomer units, and l is the length of an ethylene chain (0.154 nm). Table 1 summarizes the reaction conditions in terms of the PVP concentration; Table 2 summarizes the reaction conditions determined by the PVP molecular weight and PVP length.

Table 2
Reaction conditions and results of BT–PVP synthesis using solutions containing PVP with different molecular weights. The concentration of PVP was 50 g/L.

Sample	PVP molecular weight (g/mol)	Crystallite size ^a (nm)	Lattice parameter (Å)	Particle size ^b (nm)	PVP length (nm)	Shell thickness ^c (nm)
BT-W1	2500	45.5	4.0469	143.8	3	0.5
BT-W2	10,000	44.5	4.0428	141.0	12	4.5
BT-W3	40,000	43.1	4.0433	143.5	47	3.7
BT-W4	130,000	42.2	4.0444	151.5	152	6.2
BT-W5	360,000	42.3	4.0432	132.2	420	4.1

^a Calculated using Scherrer's equation.^b Measured by FE-SEM.^c Calculated using Eq. (2) in this paper.

2.2. Characterization

The phase and crystallinity of the prepared samples were investigated by X-ray diffraction (XRD; SmartLab, Rigaku, Japan). The morphology of the samples was observed by field-emission scanning electron microscopy (FE-SEM; JSM-700F, JEOL, Japan). Transmission electron microscope (TEM) images, high-resolution TEM (HRTEM) images, and the corresponding fast Fourier transform (FFT) patterns were obtained with a TEM (JEM-2100F, JEOL, Japan) operating at an accelerating voltage of 200 kV. Dynamic light scattering (DLS; FPAR-1000, Otsuka Electronics Co., Ltd.) was used for the evaluation of the nanoparticle size in a solvent to characterize the re-dispersion. The DLS measurements were repeated five times to estimate the re-dispersion in an aqueous suspension containing 1 wt% of dried BT–PVP nanoparticles. Thermogravimetry (TG; TG-DTA2010SA, Bruker AXS K.K., Japan) was carried out to evaluate the amount of in situ PVP coating on the surface of the as-prepared BT–PVP. The surface potential of the BT nanoparticles was analyzed by measuring the zeta potential (ELS-Z1/Z2, Otsuka Electronics Co., Ltd., Japan).

To directly observe the behavior of the BT–PVP nanoparticle suspension, a new type of sample holder—Trans-SEM—was used for the SEM measurements. The sample holder had a small chamber between two silicon nitride films, and the sample suspension was placed into this chamber. Following the procedures reported by Izu et al. [21], a 3 μL sample of the aqueous suspension of 1 wt% BT was released dropwise into the chamber. The sample holder was then set in the FE-SEM for images to be scanned by a secondary electron detector.

The BT–PVP particles in our study were assumed to adopt a core–shell structure, where the core was made of BT, and the shell was made of PVP. The thickness of PVP adsorbed on the surface of BT was calculated using the following equations [23]:

$$W_L = \frac{\left[\frac{4}{3}\pi\left(\frac{d_c}{2} + t_s\right)^3 - \frac{4}{3}\pi\left(\frac{d_c}{2}\right)^3\right] D_s}{\left[\frac{4}{3}\pi\left(\frac{d_c}{2} + t_s\right)^3 - \frac{4}{3}\pi\left(\frac{d_c}{2}\right)^3\right] D_s + \left[\frac{4}{3}\pi\left(\frac{d_c}{2}\right)^3\right] D_c} \times 100\%, \quad (2)$$

$$d_{cs} = d_c + 2t_s, \quad (3)$$

Download English Version:

<https://daneshyari.com/en/article/7897668>

Download Persian Version:

<https://daneshyari.com/article/7897668>

[Daneshyari.com](https://daneshyari.com)