Fabrication of BaTiO₃/Ag composites using uniform Ag-deposited BaTiO₃ particles

Takashi KOJIMA,[†] Masahiro SUGIHARA, Yusuke HOSOI, Naofumi UEKAWA and Kazuyuki KAKEGAWA

Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba 263-8522

Microstructure control of BaTiO₃/Ag composite was examined from the preparation stage of Ag-deposited BaTiO₃ particles. Uniform BaTiO₃ particles were prepared by hydrothermal treatment of a hydroxide gel. Then Ag nanoparticles were deposited uniformly on the BaTiO₃ particle surface by the reduction of diamminesilver (I) ions using glucose. Dense BaTiO₃/Ag composites were obtained respectively via pressureless sintering and spark plasma sintering of the Ag-deposited BaTiO₃ particles. Although the BaTiO₃ and Ag particles grew well after pressureless sintering, their grain growth was suppressed by spark plasma sintering. The Vickers hardness and dielectric constant of the composites were much higher than those of the monolithic BaTiO₃ sintered body.

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Key-words : Composite, Microstructure, Spark plasma sintering, Hydrothermal, Particle

[Received August 3, 2009; Accepted September 11, 2009]

1. Introduction

Because of an increasing demand for higher performance and miniaturization of electronic devices, improvement of dielectric ceramics' mechanical properties is required along with an improvement of their electric properties. Dispersion of metal nanoparticles into dielectric ceramics is effective not only for improving mechanical properties but also for increasing the dielectric constant. Dielectric/metal nanoparticle systems of many kinds—BaTiO₃/Ni,^{1)–5)} BaTiO₃/Ag,^{6)–14)} Pb(Zr,Ti)O₃/Ag,^{15)–19)} Pb(Zr,Ti)O₃/Pt,^{20)–23)} and others^{24)–29)}—have been reported. A typical system is the BaTiO₃/Ag particle composite; improvement of the mechanical properties and dielectric constant of BaTiO₃ was attained by the dispersion of Ag.^{6)–14)} However, those reported composites were prepared mainly via milling and sintering of a mixture of commercially available starting materials. Their microstructures were not controlled precisely. In this study, BaTiO₃/Ag composites were fabricated from the starting particle preparation stage to obtain a uniform microstructure. First, uniform BaTiO₃ particles were synthesized. Then, Ag particles were deposited on the BaTiO₃ particles. Aggregation of Ag at the sintering stage must be suppressed if Ag particles are to be deposited uniformly and fixed on the prepared BaTiO₃ particles. The composite's sintering procedure was also studied to sustain the starting particles' microstructure. Uniform BaTiO₃ particles were prepared using the “gel–sol” method, which is suitable for preparing monodispersed particles in large quantities by the hydrothermal treatment of a highly condensed metal-oxide gel.³⁰⁾ Uniform BaTiO₃ particles were reportedly obtained using this method.³¹⁾ The Ag particles were deposited on the prepared BaTiO₃ particles by reduction of the Ag complex using glucose.³²⁾ Then, the obtained Ag-deposited BaTiO₃ particles were

sintered respectively using conventional pressureless sintering (PS) and spark plasma sintering (SPS, also known as pulse electric current sintering: PECS).³³⁾ The SPS process is a pressure-assisted pulsed current sintering process. In this process, powder materials are stacked between the carbon die and punch on the sintering stage in a vacuum chamber. A pulsed direct current is applied to sinter the powder under uniaxial pressure. This procedure is known to be suitable for producing a dense sintered body of BaTiO₃ from fine starting particles.^{34)–39)} Reportedly, SPS processing is useful to sinter ceramic/metal composites without excess grain growth of the starting powders.^{40)–42)}

2. Experimental procedure

2.1 Preparation of BaTiO₃/Ag composites

Reagents used as starting materials were titanium isopropoxide, triethanolamine, barium hydroxide octahydrate, sodium hydroxide, and silver nitrate (Wako Pure Chemical Industries, Ltd.). Analytical grade metal standard solution (Wako Pure Chemical Industries, Ltd.), and nitric acid (Kanto Chemical Co., Inc.) were used for chemical analyses of the samples. Pure water used for the particle synthesis was prepared by reverse osmosis and electrodeionization (Elix System; Millipore Corp., USA). The water used for inductively coupled plasma – atomic emission spectrometry (ICP–AES) was purified further via passage through a Milli-Q[®] ultrapure water purification system (Millipore Corp., USA). The BaTiO₃ particles were prepared using hydrothermal treatment of a precursor gel. First, titanium isopropoxide was mixed with triethanolamine to a molar ratio of [titanium isopropoxide]:[triethanolamine] = 1:2. Then water and Ba(OH)₂·8H₂O were added; the respective concentrations of Ti⁴⁺ and Ba²⁺ were adjusted to 0.25 M and 1.0 M. The prepared precursor suspension was stirred magnetically at room temperature for 2 h to obtain the precursor gel. The obtained gels were treated hydrothermally at 250°C for 3 h. Then, the obtained particles were washed by centrifugation: once with diluted nitric acid for

[†] Corresponding author: T. Kojima; E-mail: tkojima@faculty.chiba-u.jp

removing the unreacted Ba and three times with water. The Ag particles were deposited on the BaTiO₃ particles by reduction of the diamminesilver (I) ion. **Figure 1** shows the preparation process of Ag-deposited BaTiO₃ particles. First, the prepared BaTiO₃ particles and AgNO₃ were added to aqueous ammonia. Their starting concentration was adjusted to 95% BaTiO₃ and 5% metal Ag by weight. Then, a glucose aqueous solution was added. At that time, the volume ratio of BaTiO₃ containing suspension to glucose aqueous solution was 4:1. Final concentrations of each material after mixing were set to 0.75 M BaTiO₃, 0.085 M AgNO₃, 0.21 M ammonia (Ag:NH₃ = 1:2.5), and 0.10 M glucose. After stirring the suspension at room temperature for 2 h, the obtained Ag-deposited BaTiO₃ particles were washed three times by centrifugation with water and then freeze-dried. The BaTiO₃/Ag composites were prepared using Ag-deposited BaTiO₃ particles via PS for 2 h or via SPS for 10 min. Before the PS, the powders were cold-isostatic pressed at 150 MPa. The heating and cooling rates of the PS were set as 5°C/min. The SPS was conducted under vacuum and a pressure of 29 MPa was loaded on the specimen. To prevent overshooting, the SPS heating rate was set as 200°C/min from room temperature to 600°C, 100°C/min from 600°C to 800°C, and 33°C/min from 800°C to the desired temperature. Then, the sample sintered by SPS was cooled by natural cooling. The samples sintered using SPS were heat-treated at 800°C for 1 h in air atmosphere for reoxidation

Fig. 1. Preparation process of Ag-deposited BaTiO₃ particles.

of BaTiO₃.

2.2 Characterization

The crystalline phases were identified using X-ray diffractometry (XRD, M18X-HF-SRA; Mac Science Company Ltd.) with Cu K α radiation with a monochromator. The yield of Ag was measured using ICP-AES (SPS 1700HVR; Seiko Instrument Inc.). To determine the amount of Ag deposited on the BaTiO₃ particles, Ag-deposited BaTiO₃ particles were dispersed in nitric acid (60–61 wt% HNO₃) and treated hydrothermally at 200°C for 24 h. The residue was washed three times by centrifugation with a small amount of 1 M nitric acid to recover the residual Ag on the residue particles. The Ag concentration of all solutions, including the nitric acid used for washing particles, was measured using ICP-AES. The sample morphology was observed using scanning electron microscopy (SEM, JSM-6330F; JEOL Ltd.). The Vickers hardness was measured using a Vickers hardness tester (AVK-A2; Akashi Corp.) at a load of 9.8 N. The dielectric properties were measured using an impedance analyzer (YH4192A; Yokogawa – Hewlett-Packard Ltd.) at 1 kHz and 1 Vrms.

3. Results and discussion

The precursor suspension of BaTiO₃ became a rigid gel by stirring at room temperature for 2 h. Results of XRD measurements show that single-phase BaTiO₃ particles were obtained by hydrothermal treatment of the precursor gel at 250°C for 3 h. **Figure 2** shows SEM images of hydrothermally prepared particles without (Fig. 2(a)) and with deposition of Ag particles (Fig. 2(b)). Uniform BaTiO₃ particles with an average size of ca. 80 nm were obtained by hydrothermal treatment of the precursor gel. The Ag particles (indicated by white arrows in Fig. 2(b)) with an average size of ca. 25 nm were deposited uniformly on the BaTiO₃ particles. Results of ICP-AES measurements show that the amount of Ag deposited on the BaTiO₃ particles was 94% of the feed amount of AgNO₃.

To determine the sintering conditions of the prepared particles,

Fig. 2. SEM images of BaTiO₃ particles: (a) without Ag deposition, (b) with Ag deposition.

Fig. 3. Fracture surfaces of BaTiO₃ sintered body prepared using PS at (a) 1100°C, (b) 1200°C, (c) 1300°C for 2 h.

Fig. 4. Fracture surfaces of BaTiO₃ sintered body prepared using SPS at (a) 900°C, (b) 950°C, (c) 1000°C for 10 min.

Fig. 5. XRD patterns of BaTiO₃/Ag composite prepared using (a) PS, (b) SPS: ○BaTiO₃, ▽Ag.

BaTiO₃ particles were sintered at various temperatures using PS or SPS. **Figure 3** shows the fracture surface of a BaTiO₃ sintered body prepared using PS. When the sintering temperature was 1100°C, densification was insufficient and large pores remained. When the sintering temperature was 1200°C and 1300°C, the sintered bodies were densified. However, the grains of the BaTiO₃ sintered at 1300°C were much larger than those that had been sintered at 1200°C. **Figure 4** shows fracture surfaces of the BaTiO₃ sintered body prepared via SPS. The grains of BaTiO₃ sintered at 900°C were as small as those of as-prepared BaTiO₃ particles, but the sintered body was insufficiently densified. The sintered bodies prepared at 950–1000°C were well densified and the grain growth of BaTiO₃ was greatly suppressed when the sintering temperature was 950°C. Results presented in Figs. 3 and 4 show that the sintering temperatures of the composite for PS and SPS were determined respectively at 1200°C and 950°C.

The Ag-deposited BaTiO₃ particles were sintered respectively via PS and SPS using the sintering conditions described above. **Figure 5** shows XRD patterns of prepared composites. Results verified that the obtained composites comprised only BaTiO₃ and metal Ag phases. **Figure 6** shows a comparison of fracture surfaces of the BaTiO₃ sintered body (prepared without deposition of Ag) and BaTiO₃/Ag composites. The Ag particles were dispersed uniformly in the BaTiO₃ matrix, irrespective of the sintering method (Figs. 6(b) and 6(d)). When the sintered bodies were prepared via PS (Fig. 6(b)), although Ag grains in the composite were much larger (80–500 nm) after sintering, they were smaller than those of other reported BaTiO₃/Ag composites.^{6)–14)} This smaller size of Ag particles is attributable to the fact that the starting Ag particles were very small, well dispersed, and fixed on the BaTiO₃ particles. The Ag particles in the composite prepared using SPS (Fig. 6(d)) were much smaller (30–180 nm) than those prepared using PS. These small Ag particles

Fig. 6. Fracture surfaces of BaTiO₃ sintered body and BaTiO₃/Ag composite: (a) BaTiO₃ (PS) and (b) BaTiO₃/Ag composite (PS), (c) BaTiO₃ (SPS), (d) BaTiO₃/Ag composite (SPS).

Table 1. Properties of Prepared BaTiO₃ Sintered Bodies and BaTiO₃/Ag Composites

	Relative density (%)	Vickers hardness (GPa)	Dielectric constant	Dissipation factor (%)	Mean grain size of Ag (nm)
BaTiO ₃ (PS)	98	2.5 (0.1)*	1890	1.8	—
BaTiO ₃ (SPS)	98	3.0 (0.5)*	1780	5.9	—
BaTiO ₃ /Ag (PS)	97	6.2 (0.3)*	3060	1.8	270
BaTiO ₃ /Ag (SPS)	99	8.7 (0.8)*	3650	9.0	96

*Numbers in parentheses represent the standard deviation

resulted from the low sintering temperature and short sintering time of SPS. **Table 1** presents properties of prepared BaTiO₃ sintered bodies and BaTiO₃/Ag composites. The Vickers hardness of the BaTiO₃ sintered bodies prepared using PS and SPS were, respectively, 2.5 GPa and 3.0 GPa. These values were lower than those reported for BaTiO₃ sintered bodies.^{38),43)} This low hardness might arise from difficulties in preparing the sintered body using fine starting particles. Small defects must exist between the BaTiO₃ grains, which might weaken the joint of each grain of the sintered body. The Vickers hardness of the BaTiO₃/Ag composites was higher than those of monolithic BaTiO₃ sintered bodies: the sample prepared via SPS showed the highest value. Panteny et al. reported that the hardness of the BaTiO₃ sintered body

increased by the addition of a small amount of Ag (up to 3.2 wt% Ag).¹²⁾ Chen et al. reported that the addition of Ag more than 1 wt% improves the BaTiO₃ sintering properties.⁹⁾ Therefore, in this case, the addition of 5 wt% Ag must improve the sinterability of BaTiO₃ particles and strengthen the grain boundary. In addition, the Ag grains in the composites were small and the composite prepared using SPS showed the highest hardness. The increased hardness might be also attributable to the decreased size of Ag grains. The Ag grains must be hardened concomitantly with their decrease in size: it enhances the pinning effect for the dislocation and sliding of BaTiO₃ grains.^{44)–46)} For this study, measurement of other mechanical properties was not conducted because the current sample size was too small. Scaling up of the particle synthesis is in progress. The dielectric constant of the monolithic BaTiO₃ sintered bodies was ca. 1800, irrespective of the sintering procedure. The dielectric constant of the BaTiO₃/Ag composites was higher than those of BaTiO₃ sintered bodies. This increase in the dielectric constant might be explained by the percolation theory.^{11),13),46)} Furthermore, the rate of increase in the dielectric constant of the BaTiO₃/5 wt% composites prepared in this study from the monolithic BaTiO₃ sintered body was larger than those of reported other BaTiO₃/5 wt% Ag composite.^{6),9)–11),13),14)} This high dielectric constant of the composite prepared in this study might be attributable to the Ag grains' small diameter. When the volume ratio of Ag in the composite is constant, the interfacial area of Ag grains increases concomitantly with their decreased diameter. This increase in interfacial area imparts a greater dipole moment to the composite overall.⁴⁷⁾ The composite prepared using SPS showed a higher dielectric constant than that prepared using PS, which might also be attributable to the further miniaturization of Ag grains. However, the dissipation factors of the sample prepared using SPS are higher than those prepared using PS, which is attributable to the reductive atmosphere of SPS. The SPS was conducted under vacuum using a carbon die. Although the reoxidation treatment was conducted in this study, it was inferred to be insufficient. The dissipation factor can be improved by controlling the reoxidation condition.

4. Conclusions

Barium titanate particles of uniform size and shape were prepared using a hydrothermal procedure. Using glucose reduction of diamminesilver (I) ion, Ag particles with an average size of ca. 25 nm were deposited uniformly on the surfaces of BaTiO₃ particles. The BaTiO₃/Ag composite, which had been fabricated by spark plasma sintering of the prepared particles, showed a uniform microstructure with small BaTiO₃ and Ag grains. The BaTiO₃/Ag composites had a higher Vickers hardness and dielectric constant (at room temp.) than those of monolithic BaTiO₃ sintered body. These higher values might be attributable to the small Ag grains dispersed in the composites.

Acknowledgment The authors thank Prof. Taro Toyoda, Prof. Masanori Fujinami, and Prof. Koichi Oguma of Chiba University for ICP–AES measurements.

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