Preparation and Microstructure of Electrospun BaTiO₃ Fibers

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Abstract. Barium titanate (BaTiO₃: BT) is widely used in various shapes depending on specific applications. Recently, 1-D ferroelectric ceramics are eagerly studied to innovate on new applications. Electrospinning is a versatile method to prepare 1-D nanomaterials. Here, we have prepared BaTiO₃/poly(vinyl alcohol) (BT/PVA) composite fibers via the electrospinning method. Suspensions of BT/PVA aq. were prepared with weight ratio of BT:PVA:H₂O = $x:0.1:0.9-x$ ($x = 0.2$ and 0.3). Dried electrospun BT/PVA fibers were sintered at 900-1000°C for 2 h in air. Morphological change of the 1-D BT fibers before and after sintering was investigated by using scanning electron microscopy (SEM) observation. Distribution of the fiber diameter before and after sintering was characterized; average diameters of the 1-D BT fibers before and after sintering were 720 nm and 640 nm, respectively.

1. Introduction

Barium titanate (BaTiO₃: BT) was first synthesized in 1940s and has been widely used as many applications because of their excellent ferroelectric properties [1-3]. The sample shape and size are very important depending on specific applications. For example, BT sheets (with micrometer-order thickness) are applied for multilayered ceramic capacitors (MLCC) and positive temperature coefficient (PTC) thermistors. BT fibers will be applied for non-volatile ferroelectric random access memories (FeRAM) and nano-electromechanical systems (NEMS) [4, 5].

There are several kinds of preparation methods for ferroelectric 1-D ceramics, *e.g.* sol-gel [6] and anodic aluminum oxide (AAO) template method [7]. In this study, we have selected an electrospinning method to prepare BT fibers. Electrospinning is typically used for the polymer-based fiber preparation, but this method can be also applicable for the ceramic fiber preparation. In this method, high electric field (~ several to tens of kV) is typically applied to a ceramics/polymer mixed solution (or suspension), as a precursor of ceramic fibers, in order to electrospray it on a metal collector. Organic-inorganic precursor solutions (such as alkoxides) have been widely used for electrospinning of ceramic fibers, due to the homogeneity and quality of final fibers [8], but the use of organic-inorganic precursor solutions is sometimes inferior in versatility.

In this study, ceramic powder suspension in a PVA solution was used to prepare BT/ PVA composite fibers. Then, the dried composite fibers were sintered to obtain BT ceramics fibers. Morphological change of the 1-D BT fibers before and after sintering was discussed by using scanning electron microscopy (SEM) observation. Distribution of the fiber diameter before and after sintering was characterized in detail.

2. Experimental procedure

A commercial BaTiO₃ powder (Fig. 1, BT-01, Sakai Chemical Industries Ltd., Osaka, Japan) and a dispersant (ammonium polyacrylate, A-6114, Toagosei Co. Ltd., Tokyo, Japan) were mixed for 5 min in distilled water with a magnet stirrer (500 rpm at room temperature). A commercial PVA powder (no.165-17915, Wako Chemical Industries Ltd., Osaka, Japan) was added into the BT aqueous suspension. The composition of BT/PVA aq. suspensions were BT:PVA:H₂O = $x:0.1:0.9-x$ ($x = 0.2$ and 0.3) in weight. The suspensions were stirred for 2 h (500 rpm at 90°C), and then, they were further stirred for 30 min at room temperature.

The BT/PVA aq. suspensions were electrospun (electric field: 10 kV, suspension flow rate: 3.4 mL/h, distance between needle-tip and metal collector: 7.5 cm) from a stainless needle (inner diameter: 0.34 mm) on an aluminum collector (Fig. 2). The electrospun fibers were dried, and then sintered at 900-1000°C for 2 h in air. Microstructural observation for electrospun fibers before and after sintering (*i.e.* BT/PVA composite fiber and BT fiber) was carried out with scanning electron microscopy (SEM, JSM-5600/SV, JEOL, Tokyo, Japan). Diameter distributions of the fibers before and after sintering were determined by an image analysis from SEM images using Image J software.

Fig. 1 SEM image of the starting BaTiO₃ powder.

Fig. 2 Schematic illustration of electrospinning equipment.

3. Results and Discussion

Figure 3 (a)-(c) show SEM images of electrospun fibers of $x = 0.2$. From Fig. 3 (a), BT/PVA composite fibers were successfully obtained by the electrospinning method; somewhat rough surface of the fibers indicate the BT particles. After the sintering at 900°C (Fig. 3 (b)), fiber morphology was almost lost due to the insufficient bonding among BT particles. On the contrary, after the sintering at 1000°C (Fig. 3 (c)), short fiber morphology still remained due to the partial bonding among BT particles. When $x = 0.3$ (Fig. 3(d)-(f)), the BT/PVA composite fibers became thicker than $x = 0.2$. Similar morphological change with sintering was observed, but much longer fibers were successfully

obtained at 1000°C (Fig. 3 (f)). These results indicate that sintering temperature of over 1000°C is needed to form continuous BT fibers. Actually, we confirmed obvious necking among BT particles (Fig. 4).

Fig. 3 SEM images of electrospun fibers: (a) before sintering ($x = 0.2$), (b) sintered at 900°C ($x = 0.2$), and (c) sintered at 1000°C ($x = 0.2$); (d) before sintering ($x = 0.3$), (e) sintered at 900°C ($x = 0.3$), and (f) sintered at 1000°C ($x = 0.3$).

Fig. 4 A SEM image of BaTiO₃ (BT-01) powder calcined at 1000°C for 2 h.

Figure 5 demonstrates the diameter distributions of BT/PVA composite fibers (i.e. before sintering) for $x=0.2$ and 0.3 . Average diameter of the fibers of $x = 0.2$ was 440 nm and those of $x = 0.3$ was 720 nm. The histogram of the fibers of $x = 0.3$ became broader than that of $x = 0.2$ fibers, and shifted to larger size. As shown in Fig. 3 (b) and (c), continuous ceramics fibers were not obtained for $x = 0.2$, either sintered at 900°C or 1000°C. Hence, to prepare continuous fibers after sintering, BT/PVA fibers with the diameter of $> 0.6 \mu\text{m}$ must be favorable, judging from Fig. 5.

Figure 6 shows histograms of the fibers of $x = 0.3$ before and after sintering. The histograms before and after sintering had similar tendency. Average diameters before and after sintering were 720 nm and 640 nm, respectively. The diameter of BT fibers derived from BT/PVA suspension in this study was almost same as that of the sol-gel derived BT fibers by electrospinning, 400-800 nm, reported by Wei et al [8]. This result suggests that preparing thick and dense pre-sintered fibers is important to obtain continuous ceramics fibers from powder suspension system.

4. Conclusions

BT/PVA composite fibers (BT:PVA:H₂O = $x:0.1:0.9-x$, $x=0.2$ and 0.3) were prepared by electrospinning method. Continuous BT ceramics fibers were successfully obtained by the sintering of BT/PVA composite fibers ($x=0.3$) at 1000°C for 2 h. The average diameters of the fibers ($x=0.3$)

before and after sintering were 720 nm and 640 nm, respectively. Throughout this study, ceramic powder suspension, instead of organic-inorganic hybrid precursor, is also effective to prepare continuous fibers, which is promising toward the reduction of the fabrication cost.

Fig. 5 Diameter distributions of BT/PVA composite fibers ($x=0.2$ and 0.3). The total sampled numbers of $x=0.2$ and 0.3 were 143 and 77, respectively.

Fig. 6 Diameter distributions of $x=0.3$ BT/PVA composite fibers (before sintering) and BT fiber sintered at 1000°C . The total sampled numbers of composite fibers and BT fibers were 77 and 127, respectively.

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